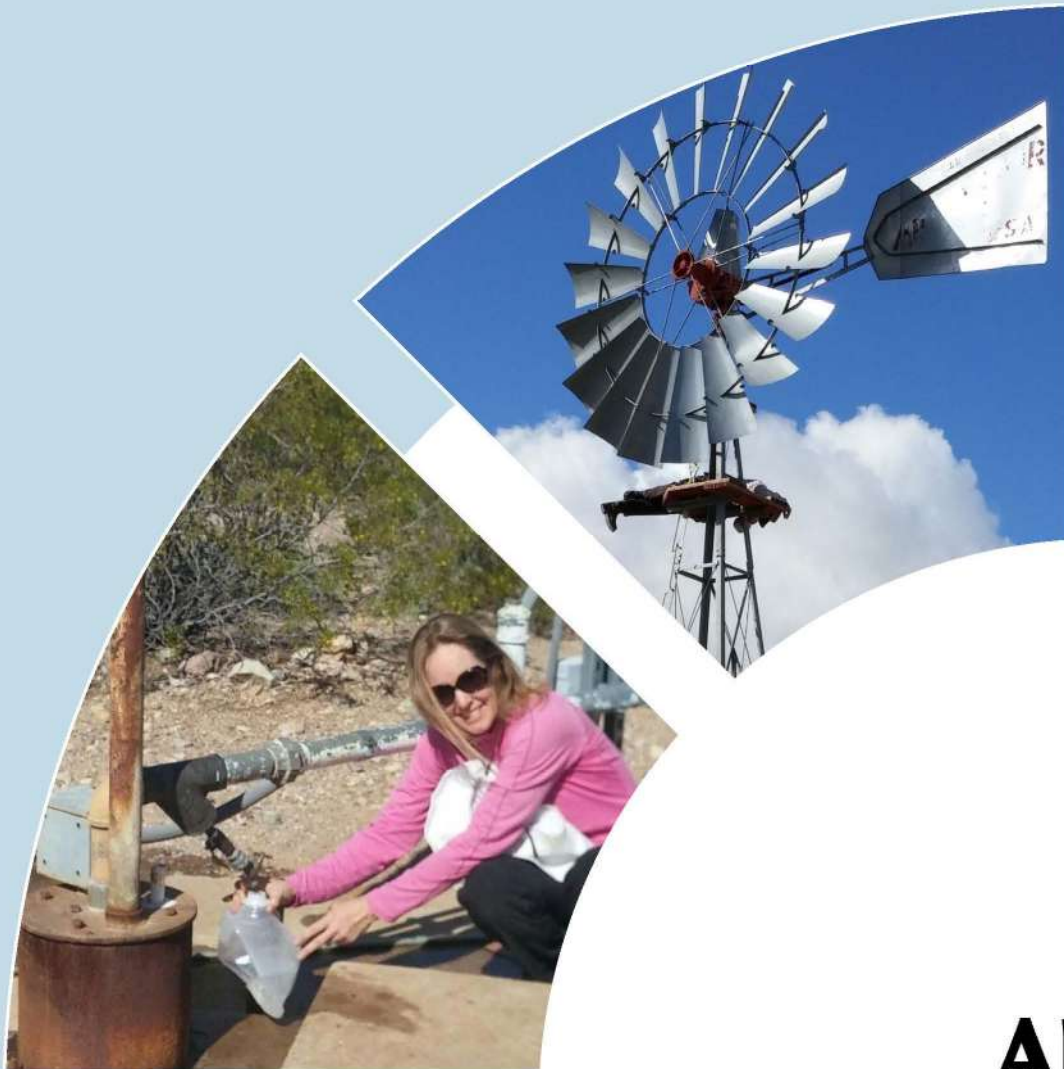


Ambient Groundwater Quality of the Western Mexican Drainage

A 2016-2017 Baseline Study

Publication Number OFR-17-02



Arizona Department of Environmental Quality
Water Quality Division
Groundwater Section
Groundwater Monitoring and Engineering Unit
1110 West Washington St.
Phoenix, Arizona 85007-2935

Ambient Groundwater Quality of the Western Mexican Drainage: A 2016-2017 Baseline Study

By Douglas C. Towne

Arizona Department of Environmental Quality Open File Report 17-02

ADEQ Water Quality Division
Groundwater Section
Groundwater Monitoring and Engineering Unit
1110 West Washington St.
Phoenix, Arizona 85007-2935

Thanks:

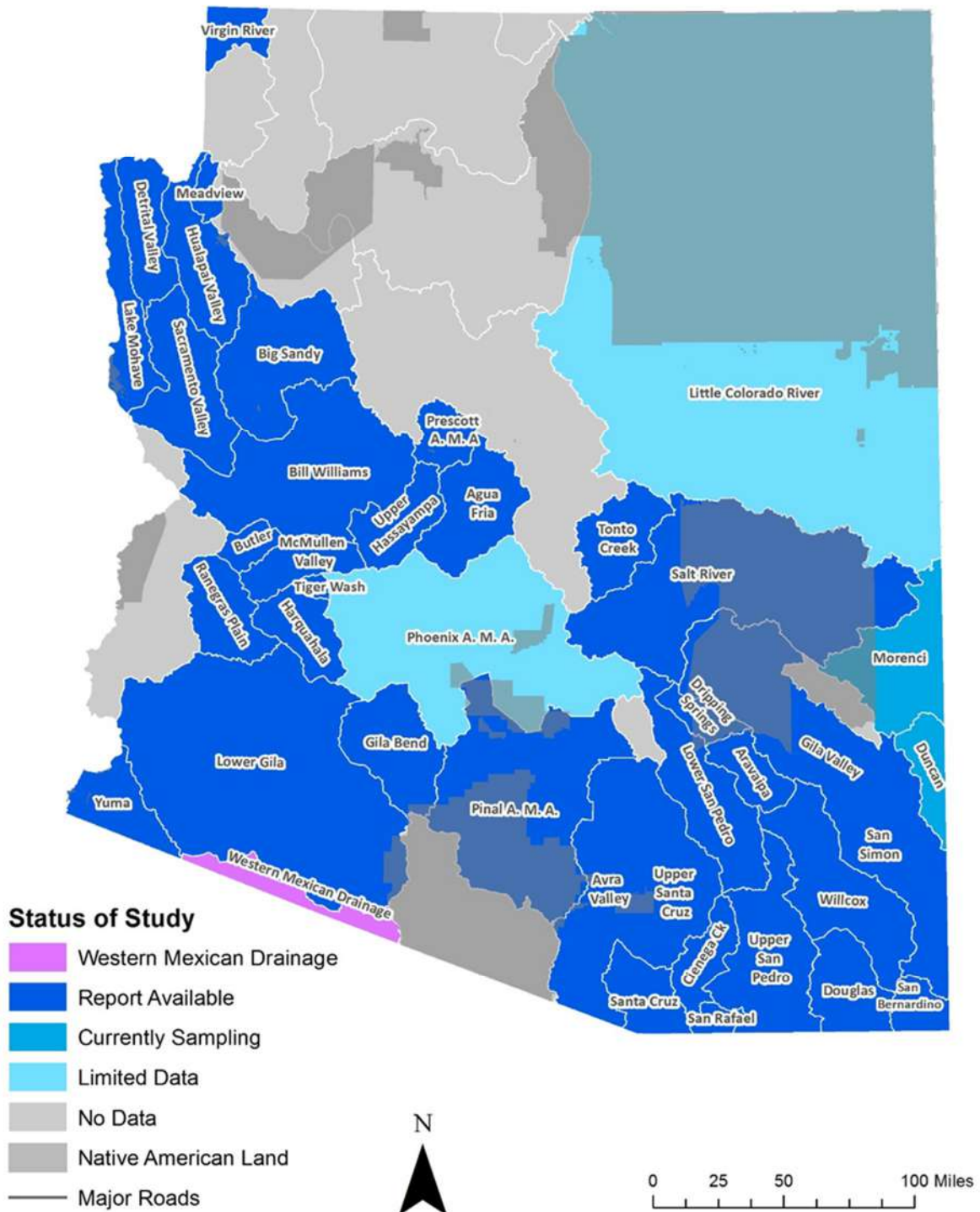
Field Assistance:	Elizabeth Boettcher. Special recognition is extended to the well owners who gave their permission to collect groundwater data.
Report Review:	Hector Alejandro Zamora
Photo Credits:	Douglas Towne

ADEQ Ambient Groundwater Quality Open-File Reports (OFR) and Factsheets (FS):

Lower Gila Basin	OFR 17-01, 74 p.	FS 17-01, 6 p.
20-Year Groundwater Quality in Arizona	OFR 16-02, 26 p.	-
Salt River Basin	OFR 16-01, 74 p.	FS 16-15, 6 p.
Gila Bend Basin	OFR 15-07, 77 p.	FS 15-05, 6 p.
Tiger Wash Basin	OFR 14-07, 33 p.	FS 14-20, 4 p.
Avra Valley Sub-basin of the Tucson AMA	OFR 14-06, 63 p.	FS 14-11, 5 p.
Harquahala Basin	OFR 14-04, 62 p.	FS 14-09, 5 p.
Tonto Creek Basin	OFR 13-04, 50 p.	FS 13-18, 4 p.
Upper Hassayampa Basin	OFR 13-03, 52 p.	FS 13-11, 3 p.
Aravaipa Canyon Basin	OFR 13-01, 46 p.	FS 13-04, 4 p.
Butler Valley Basin	OFR 12-06, 44 p.	FS 12-10, 5.p.
Cienega Creek Basin	OFR 12-02, 46 p.	FS 12-05, 4.p.
Ranegras Plain Basin	OFR 11-07, 63 p.	FS 12-01, 4.p.
15-Year Groundwater Quality in Arizona	OFR 11-04, 26 p.	-
Bill Williams Basin	OFR 11-06, 77 p.	FS 12-01, 4.p.
San Bernardino Valley Basin	OFR 10-03, 43 p.	FS 10-31, 4 p.
Dripping Springs Wash Basin	OFR 10-02, 33 p.	FS 11-02, 4 p.
McMullen Valley Basin	OFR 11-02, 94 p.	FS 11-03, 6 p.
Gila Valley Sub-basin	OFR 09-12, 99 p.	FS 09-28, 8 p.
Agua Fria Basin	OFR 08-02, 60 p.	FS 08-15, 4 p.
Pinal Active Management Area	OFR 08-01, 97 p.	FS 07-27, 7 p.
Hualapai Valley Basin	OFR 07-05, 53 p.	FS 07-10, 4 p.
Big Sandy Basin	OFR 06-09, 66 p.	FS 06-24, 4 p.
Lake Mohave Basin	OFR 05-08, 66 p.	FS 05-21, 4 p.
Meadview Basin	OFR 05-01, 29 p.	FS 05-01, 4 p.
San Simon Sub-Basin	OFR 04-02, 78 p.	FS 04-06, 4 p.
Detrital Valley Basin	OFR 03-03, 65 p.	FS 03-07, 4 p.
San Rafael Basin	OFR 03-01, 42 p.	FS 03-03, 4 p.
Lower San Pedro Basin	OFR 02-01, 74 p.	FS 02-09, 4 p.
Willcox Basin	OFR 01-09, 55 p.	FS 01-13, 4 p.
Sacramento Valley Basin	OFR 01-04, 77 p.	FS 01-10, 4 p.
Upper Santa Cruz Basin (w/ USGS)	OFR 00-06, 55 p.	-
Prescott Active Management Area	OFR 00-01, 77 p.	FS 00-13, 4 p.
Upper San Pedro Basin (w/ USGS)	OFR 99-12, 50 p.	FS 97-08, 2 p.
Douglas Basin	OFR 99-11, 155 p.	FS 00-08, 4 p.
Virgin River Basin	OFR 99-04, 98 p.	FS 01-02, 4 p.
Yuma Basin	OFR 98-07, 121 p.	FS 01-03, 4 p.

These publications are available at: www.azdeq.gov/environ/water/assessment/ambient.html

ADEQ Ambient Groundwater Reports



Contents

Abstract.....	1
Introduction	1
Purpose and Scope.....	2
Benefits of Study	2
Physical and Cultural Resources	2
Land Ownership	4
Climate	4
Groundwater Resources	4
Investigation Methods	5
Sample Collection	6
Laboratory Methods	8
Data Evaluation	8
Quality Assurance	8
Data Validation	12
Groundwater Sampling Results	13
Water Quality Standards.....	13
Analytical Results	17
Groundwater Composition	20
Oxygen, Hydrogen and Nitrogen Isotopes.....	25
Discussion.....	30
Appendices.....	32
References	39

Tables

Table 1 - Laboratory Water Methods and Minimum Reporting Levels Used in the Study.....	9
Table 2 - Laboratory Water Methods and Minimum Reporting Levels Used in the Study.....	10
Table 3 - Summary Results of Four Duplicate Samples from Test America Laboratory	12
Table 4 - Sites Exceeding Health-based Water Quality Standards or Primary MCLs	15
Table 5 - Sites Exceeding Aesthetics-based Water Quality Guidelines/Secondary MCLs.....	16
Table 6 - Summary Statistics for Groundwater Quality Data update after final trip	18
Table 7 - Summary Statistics for Groundwater Quality Data.....	19
Table 8 - Sodium and Salinity Hazards for Sample Sites	22
Table 9 - Water Quality Standard Exceedances by Recharge Source	35

Figures

Figure 1 - Geography of the Western Mexican Drainage basin.....	3
Figure 2 - The basin consists almost entirely of federal land used for wildlife, recreation, and military purposes.....	4
Figure 3 - Organ Pipe Cactus National Monument comprises the eastern one-third of the basin.	5
Figure 4 - The Cabeza Prieta National Wildlife Refuge comprises two-thirds of the basin.	6
Figure 5 - El Camino del Diablo connects Papago Well to Tule Well	7
Figure 6 - The well that supplies Gringo Pass Motel was one of two sites sampled in Lukeville	8
Figure 7 - ADEQ's Elizabeth Boettcher collects a sample (WMD-2) from Dripping Spring in the Organ Pipe Cactus National Monument	11
Figure 8 - Water Quality of the Western Mexican Drainage basin.....	14
Figure 9 - ADEQ's Elizabeth Boettcher admiring Quitobaquito Spring in the Organ Pip Cactus National Monument.	17
Figure 10 - Samples collected in the basin are predominantly of sodium-mixed chemistry.....	20
Figure 11 -Water chemistry of the Western Mexican Drainage basin.	21
Figure 12 - TDS concentrations in the Western Mexican Drainage basin	23
Figure 13 - Hardness concentrations in the Western Mexican Drainage basin.	24
Figure 14 - Evaporation line for the basin.....	20
Figure 15 - Evaporation lines from ADEQ Ambient Groundwater Studies in Arizona.	26
Figure 16 - Recharge source of samples in the Western Mexican Drainage basin.....	27
Figure 17 - Nitrate-Nitrogen-15 Relationship.	28
Figure 18 - Nitrate concentrations in the Western Mexican Drainage basin.	29
Figure 19 - Papago Windmill, located by the O'Neill Hills within the Cabeza Prieta National Wildlife Refuge, was the only sample site (WMD-8) to meet all water quality standards.	30
Figure 20 - Arsenic concentrations in the Western Mexican Drainage basin.....	31
Figure 21 - Most of the Western Mexican Drainage basin is so remote, water sources such as Papago Well are major landmarks.....	32
Figure 22 - Fluoride concentrations in the Western Mexican Drainage basin	33

Figure 23 - Quitobaquito Spring is just across the international border, which parallels Mexican Highway 2 at this location.....	34
Figure 24 - ADEQ's Elizabeth Boettcher samples South Well #4 used for public water supply at the Organ Pipe Cactus National Monument.....	35

Abbreviations

amsl	above mean sea level
ac-ft	acre-feet
af/yr	acre-feet per year
ADEQ	Arizona Department of Environmental Quality
ADHS	Arizona Department of Health Services
ADWR	Arizona Department of Water Resources
AMA	Active Management Area
ARRA	Arizona Radiation Regulatory Agency
AZGS	Arizona Geological Survey
As	arsenic
bls	below land surface
BLM	U.S. Department of the Interior Bureau of Land Management
°C	degrees Celsius
CI _{0.95}	95 percent Confidence Interval
Cl	chloride
EPA	U.S. Environmental Protection Agency
F	fluoride
Fe	iron
gpm	gallons per minute
HCl	hydrochloric acid
LLD	Lower Limit of Detection
Mn	manganese
MCL	Maximum Contaminant Level
ml	milliliter
msl	mean sea level
ug/L	micrograms per liter
um	micron
μS/cm	microsiemens per centimeter at 25° Celsius
mg/L	milligrams per liter
MRL	Minimum Reporting Level
ns	not significant
ntu	nephelometric turbidity unit
pCi/L	picocuries per liter
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
SAR	Sodium Adsorption Ratio
SDW	Safe Drinking Water
SC	Specific Conductivity
su	standard pH units
SO ₄	sulfate
TDS	Total Dissolved Solids
TKN	Total Kjeldahl Nitrogen
USFS	U.S. Forest Service
USGS	U.S. Geological Survey
VOC	Volatile Organic Compound
WMD	Western Mexican Drainage basin
WQARF	Water Quality Assurance Revolving Fund
*	significant at $p \leq 0.05$ or 95% confidence level
**	significant at $p \leq 0.01$ or 99% confidence level

Abstract

The Arizona Department of Environmental Quality (ADEQ) conducted a baseline groundwater quality study of the Western Mexican Drainage basin located along the International Boundary with Mexico in southwestern Arizona. The basin comprises 610 square miles within Yuma and Pima counties and consists of desert valleys surrounded by low elevation mountains.¹ The basin is a thin strip of land, no more than 15 miles wide, along the international boundary with Mexico. The majority of the Western Mexican Drainage basin lies within Mexico.

Land ownership consists of federal lands (99 percent) including the Cabeza Prieta National Wildlife Refuge, and the Organ Pipe Cactus National Monument. Less than one percent of the basin consists of Tohono O'odham Indian tribal land, State Trust land, and private land, the latter located near Lukeville.²

All natural waterways are ephemeral, and there are only a few perennial springs, including Quitobaquito Spring within the Organ Pipe Cactus National Monument. Groundwater occurs primarily in the basin fill, but there is little-detailed information available about the aquifer. The basin fill is composed of the erosional remnants of nearby mountains and consist of unconsolidated gravel, sand, silt, and clay. Groundwater flows from north to south into Mexico, with 2,400 acre-feet crossing the border annually.³

ADEQ sampled seven sites consisting of five wells and two springs in the basin. Inorganic constituents and isotopes of oxygen, deuterium, and nitrogen were collected at all sites, while fewer samples were collected for radon (five) radionuclide (four) sites.

Of the seven sites sampled, three sites exceeded health-based, Primary Maximum Contaminant Levels (MCLs). Primary MCLs were exceeded for arsenic (three sites), fluoride (three sites), and uranium (one site). These are enforceable standards for drinking water purposes supplied by a public water system.⁴ Eight sites exceeded aesthetics-based, Secondary MCLs. Constituents exceeded include fluoride (four sites) total dissolved solids (TDS) (three sites) and at one site apiece for aluminum, chloride, iron, manganese, and sulfate. One site met all drinking water quality standards. Groundwater is commonly sodium-mixed chemistry, slightly-alkaline, fresh, and moderately hard.^{5 6}

Stable isotopes of oxygen-18 and hydrogen values at sample sites reflect recharge from local precipitation. Four of the samples, however, collected in Organ Pipe Cactus National Monument and Lukeville are less evaporated. This indicates the recharge also consists of underflow from precipitation that occurred in the higher-elevation headwaters of the Rio Sonoyta, either in the Sierra de El Cobre in Sonora, Mexico or from the Baboquivari Range in the eastern part of the Tohono O'odham Nation.

These less evaporated sites include Quitobaquito Spring, which confirms the contribution of water from the regional aquifer located across the border in Mexico to the spring's flow.⁷ The additional information about the source of Quitobaquito Spring suggests that Organ Pipe Cactus National Monument should monitor groundwater withdrawals in Mexico to assure the vital water source's continued viability.

Introduction

Purpose and Scope

The Western Mexican Drainage basin comprises 610 square miles in southwestern Arizona within Yuma and Pima counties (Figure 1).⁸ The basin extends from east of Lukeville, northwest along the International Border with Mexico past the Tule Desert. Only the upper portions of the Western Mexican Drainage groundwater basin are within Arizona, as the majority of the basin lies within Mexico.

The basin includes the border community of Lukeville.⁹ Land is used for primarily for wildlife and recreation uses.

The basin is physically characterized by desert plains and valleys surrounded by low elevation mountains. Groundwater is predominantly pumped for public water supply in Lukeville and in the Organ Pipe Cactus National Monument.

There are several perennial springs on the national monument including Quitobaquito Spring, an oasis which is one of the most important ecological and cultural water sources in the Sonoran Desert.¹⁰

Sampling by the Arizona Department of Environmental Quality (ADEQ) Ambient Groundwater Monitoring program is authorized by legislative mandate in the Arizona Revised Statutes §49-225, specifically: *"...ongoing monitoring of waters of the state, including...aquifers to detect the presence of new and existing pollutants, determine compliance with applicable water quality standards, determine the effectiveness of best*

*management practices, evaluate the effects of pollutants on public health or the environment, and determine water quality trends."*¹¹

Benefits of Study

This study is designed to provide the following benefits:

- Characterizing regional groundwater quality conditions in the Western Mexican Drainage basin.
- Identifying further groundwater quality research needs.

Physical and Cultural Resources

Geography

The Western Mexican Drainage basin is located within the Basin and Range physiographic province in southwestern Arizona. The basin's boundaries are formed by a drainage divide to the north and the International Border with Mexico on the south.

Major physiographic areas within the basin include the Ajo Mountains in the northeast, La Abra Plain west of Lukeville, and the Tule and Lechuguilla deserts in the western portion of the basin. Small portions of the Ague Dulce, Bates, Cabeza Prieta, Puerto Blanco, Sierra Pina and Tule mountains along with the Cipriano and Quitobaquito hills are found within the basin.

Elevations range from 4,024 feet above mean sea level (amsl) in the Ajo Mountains to 680 feet amsl at Las Playas at the International boundary near the center of the basin.

Vegetation types in the basin include Lower Colorado River Valley and Arizona upland Sonoran desert scrub.

Map 1 - Western Mexican Drainage Basin

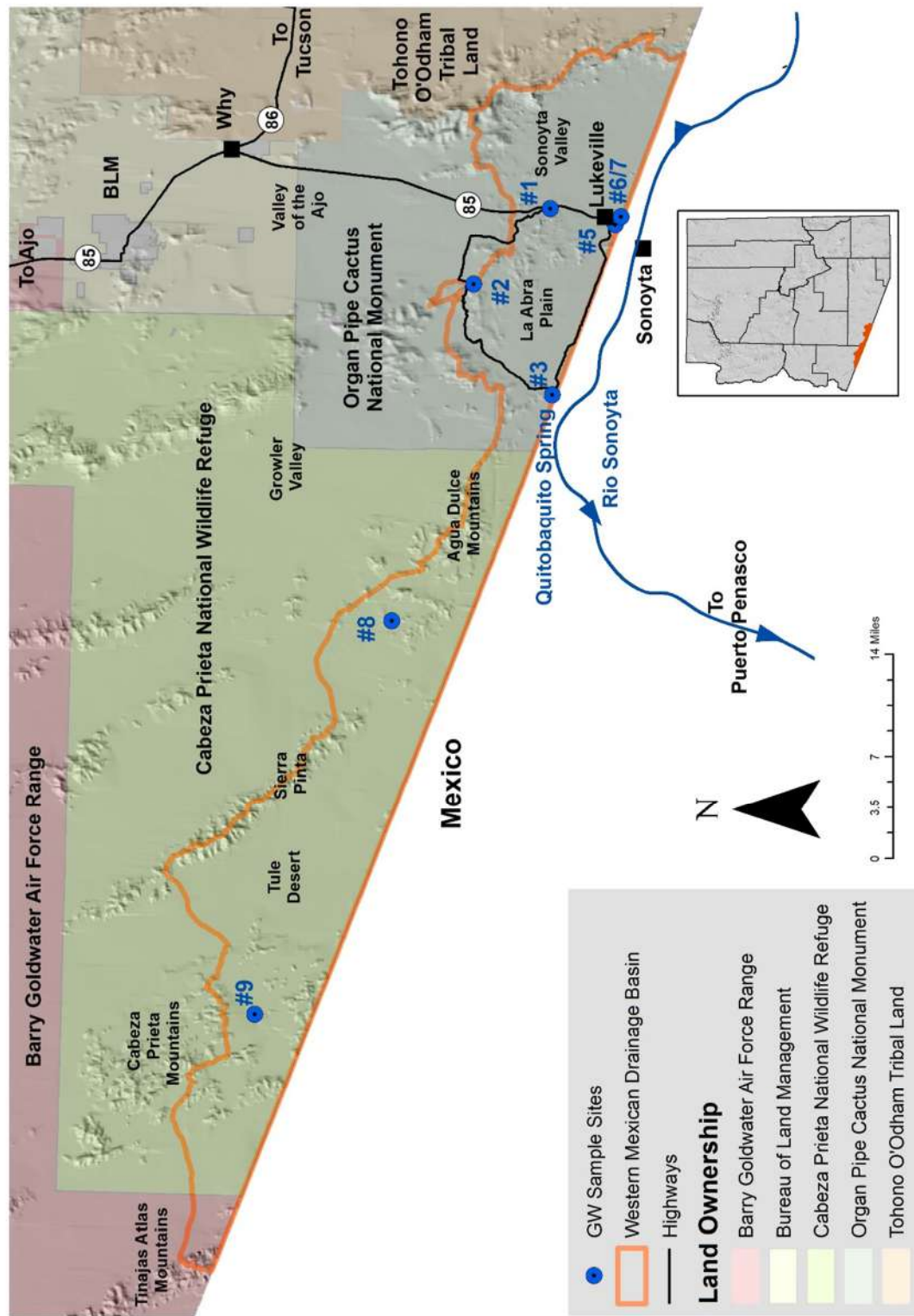


Figure 1 – Geography of the Western Mexican Drainage basin.

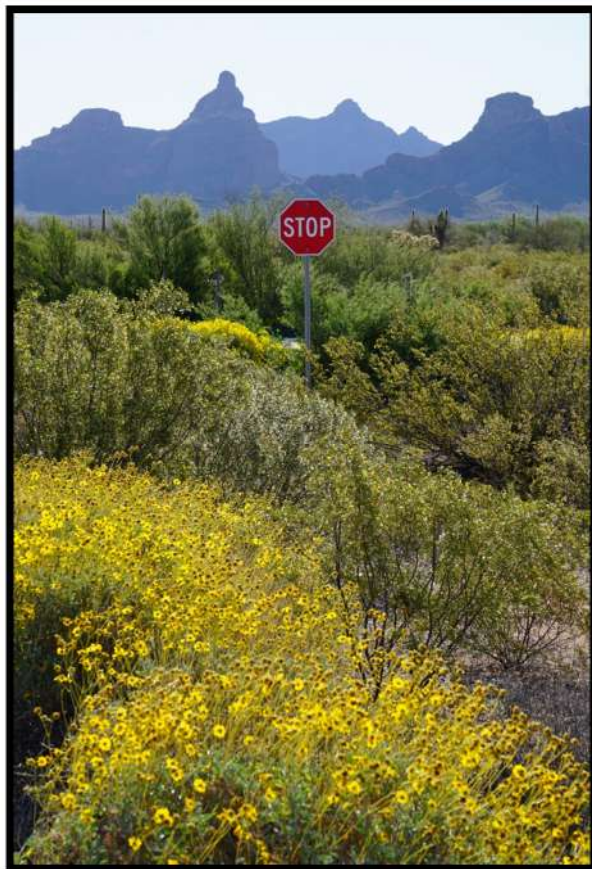


Figure 2 – The basin consists almost entirely of federal land used for wildlife, recreation, and military purposes.

Land Ownership

Land ownership consists of predominantly federal lands (99 percent) used for several purposes (Figure 2).

Federal lands managed by the U.S. Fish and Wildlife Service manage 61 percent of the basin in Cabeza Prieta National Wildlife Refuge (NWR). The National Park Service manages 36 percent of the basin as the Organ Pipe Cactus National Monument. The remaining two percent of federal lands are managed by the U.S. Military as the Barry Goldwater Air Force Range.

The remaining 0.4 percent of the basin is composed of tribal ownership by the Tohono O’odham Nation, State Trust lands, and private lands.¹²

Climate

Precipitation in the Western Mexican Drainage basin varies from almost 14 inches in the higher elevations of Organ Pipe Cactus National Monument to just above four inches in most of the low-elevation western portions.¹³ Precipitation is heaviest in July and August with late summer thunderstorms. The winter months typically have moderate amounts of precipitation. These low-intensity winter storms provide more infiltration than the intense, monsoon thunderstorms that produce large amounts of runoff.

Surface Water Resources

There are no perennial or intermittent streams in the Western Mexican Drainage basin. The basin’s largest drainage is the ephemeral Aguajita Wash located west of Lukeville in the Organ Pipe Cactus National Monument.

There are several perennial springs on the national monument including Quitobaquito Spring, an oasis which is one of the most important ecological and cultural water sources in the Sonoran Desert. Quitobaquito Spring discharges at an average rate of 28 gallons per minute (gpm) with groundwater that originates from a fault in the granite-gneiss cliffs of the adjacent Quitobaquito Hills.¹⁴

This “fissure spring” has its source located below the local water table. Once on the surface, the spring water flows through a series of small ditches into a shallow pool known as Quitobaquito Oasis, which is home to the

endangered Quitobaquito Pupfish and Sonoran Mud Turtle.¹⁵

Groundwater Resources

The Western Mexican Drainage basin is located within the Basin and Range physiographic province, which is characterized by broad alluvial-filled valleys that are dissected by elongated mountain ranges.

In the basin, the mountains are composed of igneous, metamorphic, and sedimentary rocks and the valleys contain their erosional remnants. The main water-bearing strata in the basin are composed of these unconsolidated gravel, sand, silt, and clay deposits.

Specific information about groundwater resources is sparse as there has been little groundwater development in the basin. The limited data indicate that in the basin-fill, the median well production is 50 gpm and, at least

near Lukeville, depth to water is generally less than 100 feet bls. The mountains are, generally, void of groundwater.¹⁶

The Arizona Department of Water Resources (ADWR) estimates there is approximately 4.1 million acre-feet in storage to a depth of 1,200 feet bls. An estimated 2,400 acre-feet of groundwater flow annually into Mexico. The estimated amount of groundwater pumped in the basin is low, averaging 220 acre-feet in 1985.¹⁷

Investigation Methods

ADEQ sampled seven sites, five wells and two springs to characterize the regional groundwater quality in the Western Mexican Drainage basin (Figure 8). The following types and numbers of samples were collected:



Figure 3 – Organ Pipe Cactus National Monument comprises the eastern one-third of the Western Mexican Drainage basin.



Figure 4 - The Cabeza Prieta National Wildlife Refuge comprises two-thirds of the basin.

- Inorganics at seven sites,
- Stable isotopes of oxygen, deuterium, and nitrogen at seven sites, and
- Radon at five sites, and
- Radionuclides at four sites.

Submersible pumps were used at each of the five wells.

Each well was evaluated before sampling to determine if it met ADEQ requirements. A well was considered suitable for sampling when the following general conditions were met: the owner had given permission to sample, a sampling point existed near the wellhead, and

the well casing and surface seal appeared to be intact and undamaged.¹⁸

Additional information on groundwater sample sites compiled from the Arizona Department of Water Resources (ADWR) well registry is available in Appendix A.

Sample Collection

The sample collection methods for this study conformed to the Quality Assurance Project Plan (QAPP)¹⁹ and the Field Manual for Water Quality Sampling.²⁰ While these sources should be consulted as references to specific sampling questions, a brief synopsis of the sample collection procedures is provided.

After obtaining permission from the well owner, the volume of water needed to purge the well three borehole volumes was calculated from well log and on-site information. Physical parameters: temperature, pH, and specific conductivity (SC), were monitored approximately every five minutes using a YSI multi-parameter instrument.

To assure obtaining fresh water from the aquifer, after pumping three bore volumes and physical parameter measurements were stabilized within 10 percent, a sample representative of the aquifer was collected from a point as close to the wellhead as possible. In some instances, it was not possible to purge three bore volumes. In these cases, at least one bore volume was evacuated, and the physical parameters had stabilized within 10 percent.

Sample bottles were labeled with the Western Mexican Drainage basin prefix (WMD) and filled in the following order based on their volatility:

- Radon
- Inorganics
- Radionuclides
- Isotopes

Radon, a naturally occurring, intermediate breakdown from the radioactive decay of uranium-238 to lead-206, was collected in two unpreserved, 40 ml clear glass vials. Radon samples were filled to minimize volatilization and sealed so that no headspace remained.²¹

The inorganic constituents were collected in three, one-liter polyethylene bottles. Samples to be analyzed for dissolved metals were filtered into a bottle using a positive-pressure

filtering apparatus with a 0.45 micron (μm) pore-size groundwater capsule filter and preserved with 5 ml nitric acid (70 percent). Samples to be analyzed for nutrients were preserved with 2 ml sulfuric acid (95.5 percent). Samples to be analyzed for other inorganic parameters were unpreserved.²²

Radiochemistry samples were collected in a collapsible four-liter plastic container.²³

Oxygen and hydrogen isotope samples were collected in a 250 ml polyethylene bottle with no preservative or refrigeration. Nitrogen isotope samples were collected in a 500 ml polyethylene bottle and filled $\frac{3}{4}$ full to allow room for expansion when frozen.²⁴



Figure 5 - El Camino del Diablo, or "the Devil's Highway" connected Papago Well to Tule Well (shown above) in the Cabeza Prieta National Wildlife Refuge.

All samples were kept at 4 degrees Celsius with ice in an insulated cooler, except the radionuclide, and oxygen and hydrogen isotope samples. Nitrogen samples were frozen upon returning from the field and maintained in that manner until submitted to the laboratory.²⁵

Chain of custody procedures were followed in sample handling. Samples for this study were collected during three field trips conducted between February 2016 and February 2017.

Laboratory Methods

Inorganic analyses for the study were conducted by Test America Laboratory of Phoenix, Arizona. A complete listing of inorganic parameters, including laboratory method and Minimum Reporting Level (MRL) is provided in Table 1 and Table 2.

Radionuclide and radon analyses were conducted by the Radiation Safety Engineering, Inc. Laboratory in Chandler, Arizona.

Isotope samples were analyzed by the Laboratory of Isotope Geochemistry at the University of Arizona in Tucson, Arizona.

Data Evaluation

Quality Assurance

Quality-assurance (QA) procedures were followed, and quality-control (QC) samples were collected to quantify data bias and variability for the Western Mexican Drainage basin study. The design of the QA/QC plan was based on recommendations provided in the *Quality Assurance Project Plan (QAPP)*²⁶ and the *Field Manual for Water Quality Sampling*.²⁷

Duplicate Samples

Duplicates are identical sets of samples collected from the same source at the same

time and submitted to the same laboratory with different identification numbers, dates, and times. Data from duplicate samples provide a measure of variability from the combined effects of field and laboratory procedures.²⁸

Duplicate samples were collected from sampling sites that were believed to have elevated or unique constituent concentrations as evaluated by SC and pH field values.



Figure 6 - The well that supplies Gringo Pass Motel (WMD-7) was one of two sites sampled in the border community of Lukeville.

Table 1 - Laboratory Water Methods and Minimum Reporting Levels Used in the Study

Constituent	Instrumentation	Test AM Water Method	Test AM Minimum Reporting Level
Physical Parameters and General Mineral Characteristics			
Alkalinity	Electrometric Titration	SM 2320B	6
SC (µS/cm)	Electrometric	SM 2510 B	2
Hardness	Calculation	SM 2340B	13
pH (su)	Electrometric	SM 4500H+	1.68
TDS	Gravimetric	SM 2540C	20
Major Ions			
Calcium	ICP-AES	EPA 200.7	1
Magnesium	ICP-AES	EPA 200.7	1
Sodium	ICP-AES	EPA 200.7	0.5
Potassium	Flame AA	EPA 200.7	0.5
Bicarbonate	Calculation	SM 2320B	6
Carbonate	Calculation	SM 2320B	6
Chloride	Potentiometric Titration	EPA 300.0	2
Sulfate	Colorimetric	EPA 300.0	2
Nutrients			
Nitrate as N	Colorimetric	EPA 300.0	0.1
Nitrite as N	Colorimetric	EPA 300.0	0.1
Ammonia	Colorimetric	SM 4500NH-3D	0.05
TKN	Colorimetric	EPA 351.2 / SM 4500	0.2
Total Phosphorus	Colorimetric	EPA 365.4 / SM 4500	0.1

All units mg/L unless noted otherwise

Table 2 - Laboratory Water Methods and Minimum Reporting Levels Used in the Study

Constituent	Instrumentation	Test AM Water Method	Test AM Minimum Reporting Level
Trace Elements			
Aluminum	ICP-AES	EPA 200.7	0.2
Antimony	Graphite Furnace AA	EPA 200.8	0.0001
Arsenic	Graphite Furnace AA	EPA 200.8	0.0005
Barium	ICP-AES	EPA 200.8	0.002
Beryllium	Graphite Furnace AA	EPA 200.7	0.005
Boron	ICP-AES	EPA 200.7	0.1
Cadmium	Graphite Furnace AA	EPA 200.8	0.5
Chromium	Graphite Furnace AA	EPA 200.8	0.002
Copper	Graphite Furnace AA	EPA 200.8	0.0005
Fluoride	Ion Selective Electrode	EPA 300.0	0.1
Iron	ICP-AES	EPA 200.7	0.2
Lead	Graphite Furnace AA	EPA 200.8	0.005
Manganese	ICP-AES	EPA 200.7	0.15
Mercury	Cold Vapor AA	EPA 245.1	0.0002
Nickel	ICP-AES	EPA 200.7	0.005
Selenium	Graphite Furnace AA	EPA 200.8	0.001
Silver	Graphite Furnace AA	EPA 200.8	0.002
Strontium	ICP-AES	EPA 200.7	0.01
Thallium	Graphite Furnace AA	EPA 200.8	0.002
Zinc	ICP-AES	EPA 200.8	0.0125
Radionuclides			
Gross alpha (activity)	Gas flow counter	EPA 600 / 00.02	1
Gross alpha (adjusted)	Gas flow counter	EPA 600 / 00.02	1
Radon	Liquid scantill. counter	7500-Rn	1
Uranium (activity)	ICP-AES	EPA 00.07	1
Uranium (adjusted)	ICP-AES	EPA 00.07	1

All units mg/L unless noted otherwise

One duplicate sample was collected for this study. The analytical results were evaluated by examining the variability in constituent concentrations regarding absolute levels and as the percent difference.

Analytical results from the Test America laboratory duplicate sample indicates that of the 40 constituents examined, 21 had concentrations above the MRL. The duplicate samples had a maximum variation or percent difference between constituents less than three percent. The only constituent exceeding this level was zinc (11 percent) and copper (22 percent) (Table 3).

Data Validation

The analytical work for this study was subjected to four QA/QC correlations.

Cation/Anion Balances

Water samples should theoretically exhibit electrical neutrality. Therefore, the sum of milliequivalents per liter (meq/L) of cations should equal the sum of meq/L of anions. However, this neutrality rarely occurs due to unavoidable variation inherent in all water quality analyses. Still, if the cation/anion balance is found to be within acceptable limits, it can be assumed there are no gross errors in concentrations reported for major ions.²⁹

Overall, cation/anion meq/L balances of Western Mexican Drainage basin samples were significantly correlated (regression analysis, $p \leq 0.01$). Of the seven samples, all were within ± 12 percent, and five samples were within ± 5 percent. The highest variation was 12 percent at WMD-8. Four samples had low cation/high anion sums while three samples had high cation/low anion sums.

SC-TDS Correlations and Ratio

Specific conductivity measured both in the field and in the lab was significantly correlated with total dissolved solids (TDS) concentrations measured by contract laboratories (regression analysis, $r = 0.99$, $p \leq 0.01$).

Specific conductivity measured by laboratories was significantly correlated with TDS concentrations measured by laboratories (regression analysis, $r = 0.99$, $p \leq 0.01$).

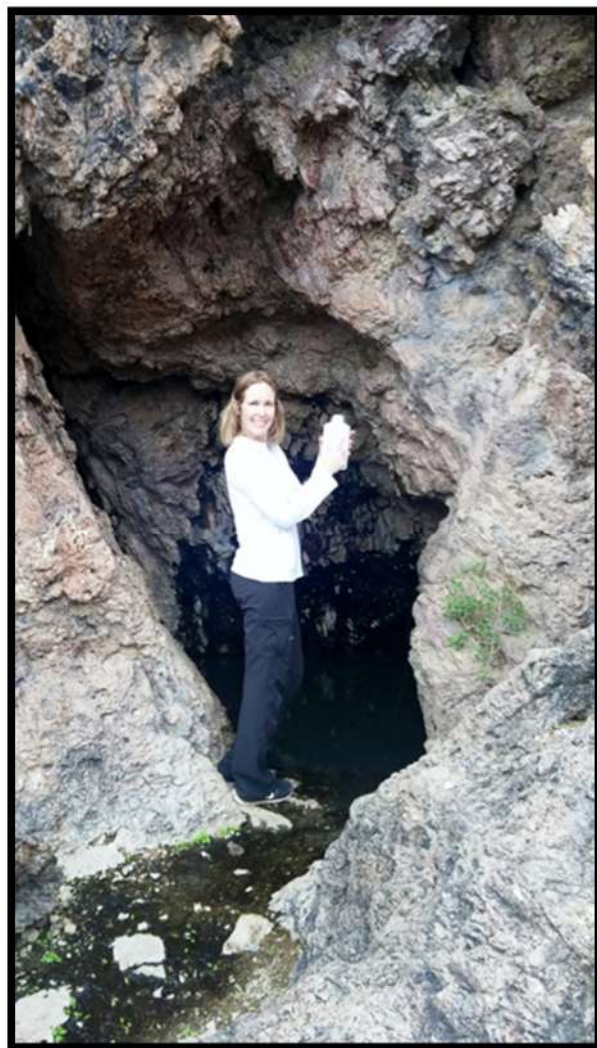


Figure 7 - ADEQ's Elizabeth Boettcher collects a sample (WMD-2) from Dripping Springs in the Organ Pipe Cactus National Monument.

Table 3 - Summary Results of One Duplicate Sample from Test America Laboratory

Parameter	Number of Duplicate Samples	Difference in Percent	Difference in Concentrations
General Mineral Characteristics			
Alk., Total	1	3 %	10
SC (µS/cm)	1	0 %	0
Hardness	1	1 %	1
pH (su)	1	1 %	0.1
TDS	1	0 %	0
Major Ions			
Calcium	1	0 %	0
Magnesium	1	1 %	0.1
Sodium	1	0 %	0
Potassium	1	2 %	0.1
Chloride	1	0 %	0
Sulfate	1	0 %	0
Nutrients			
Nitrate (as N)	1	0 %	0
Trace Elements			
Arsenic	1	0 %	0
Barium	1	2 %	0.001
Boron	1	1 %	0.01
Chromium	1	0 %	0
Copper	1	22 %	0.0008
Fluoride	1	0 %	0
Selenium	1	0 %	0
Strontium	1	0 %	0
Zinc	1	11 %	0.007

All concentration units are mg/L except as noted with certain physical parameters.

The TDS concentration in mg/L should be from 0.55 to 0.75 times the SC in $\mu\text{S}/\text{cm}$ for groundwater up to several thousand TDS mg/L. The relationship of TDS to SC becomes undefined with very high or low concentrations of dissolved solids.³⁰ Groundwater high in bicarbonate and chloride will have a multiplication factor near the lower end of this range; groundwater high in sulfate may reach or even exceed the higher factor.³¹ All seven samples were within this ratio.

SC Correlation

The SC measured in the field at the time of sampling was significantly correlated with the SC measured by contract laboratories (regression analysis, $r = 0.99$, $p \leq 0.01$).

pH Correlations

The pH values measured in the field using a YSI meter at the time of sampling were not significantly correlated with laboratory pH values.

Data Validation Conclusions

Based on the results of the four QA/QC checks, the groundwater quality data collected for the study was considered valid.

Groundwater Sampling Results

Water Quality Standards

The ADEQ ambient groundwater program characterizes regional groundwater quality. An important determination ADEQ makes concerning the collected samples is how the analytical results compare to various drinking water quality standards. ADEQ used three sets of drinking water standards that reflect the best current scientific and technical judgment available to evaluate the suitability of groundwater for drinking water use:

Federal Safe Drinking Water Act (SDWA) Primary Maximum Contaminant Levels (MCLs):

These enforceable health-based standards establish the maximum concentration of a constituent allowed in water supplied by public systems.³²

State of Arizona Aquifer Water Quality Standards:

These apply to aquifers that are classified for drinking water protected use. All aquifers within Arizona are currently classified and protected for drinking water use. These enforceable state standards are identical to the federal Primary MCLs except for arsenic which is at 0.05 mg/L compared with the federal Primary MCL of 0.01 mg/L.³³

Federal SDWA Secondary MCLs:

These non-enforceable aesthetics-based guidelines define the maximum concentration of a constituent that can be present without imparting an unpleasant taste, color, odor, or other aesthetic effects on the water.³⁴

Health-based drinking water quality standards (such as Primary MCLs) are based on the lifetime consumption (70 years) of two liters of water per day and, as such, are chronic rather than acute standards.³⁵ Specific constituent concentrations for each groundwater site are in Appendix B.

Overall Results

The seven sites sampled in the Western Mexican Drainage basin study had the following water quality results:

All health-based and aesthetics-based water quality standards were met at one site (14 percent). Health-based water quality standards were exceeded at three sites (43 percent). Aesthetics-based water quality standards were exceeded at three sites (43 percent).

Map 2 - Water Quality

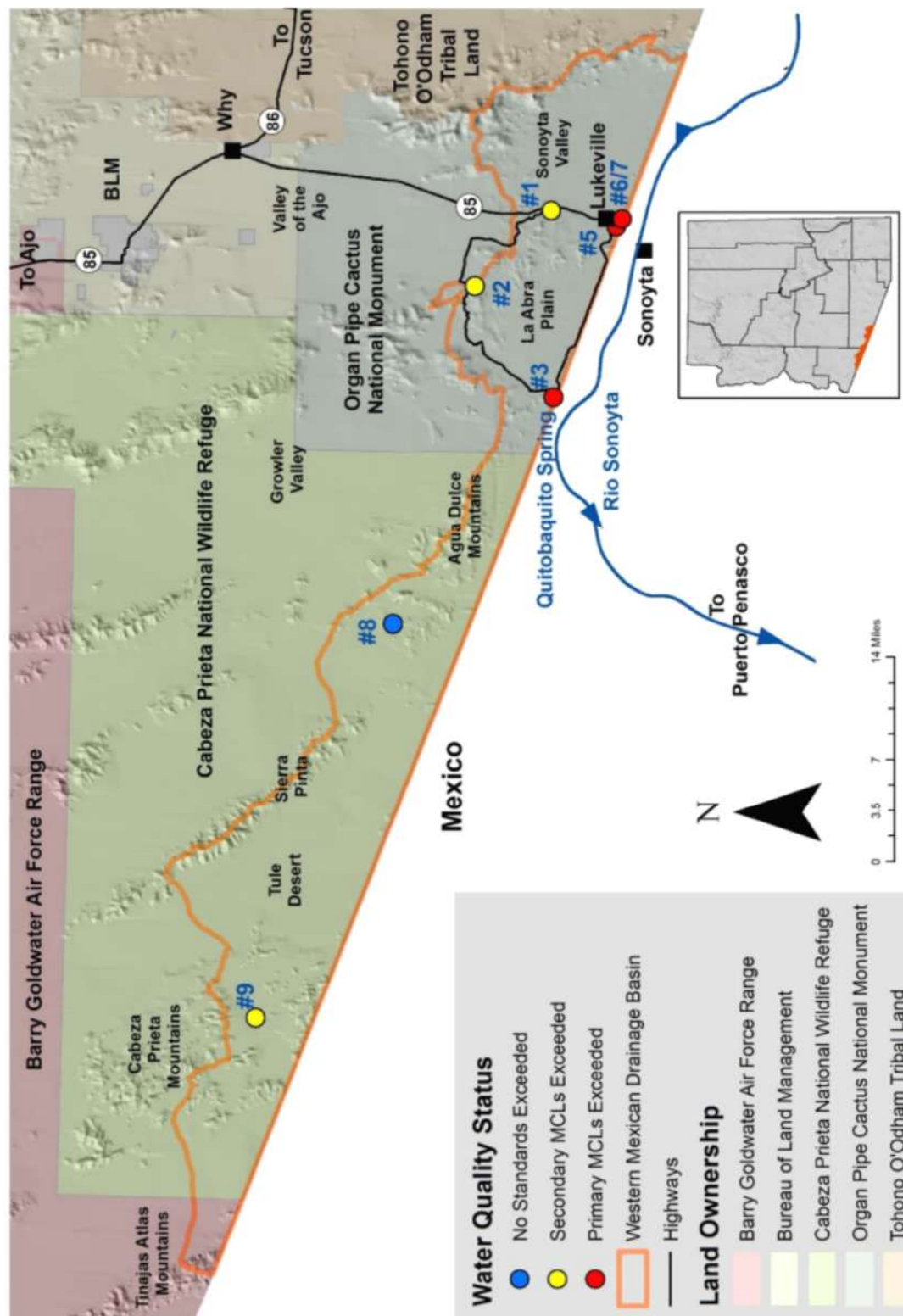


Figure 8 - Water Quality of the Western Mexican Drainage basin.

Table 4 - Sites Exceeding Health-based Water Quality Standards or Primary MCLs

Constituent	Primary MCL	Number of Sites Exceeding Primary MCL	Maximum Concentration	Potential Health Effects of MCL Exceedances *
Nutrients				
Nitrite (NO ₂ -N)	1.0	0	-	-
Nitrate (NO ₃ -N)	10.0	0	-	-
Trace Elements				
Antimony (Sb)	0.006	0	-	-
Arsenic (As)	0.01	3	0.029	dermal and nervous system toxicity
Arsenic (As)	0.05	0	-	-
Barium (Ba)	2.0	0	-	-
Beryllium (Be)	0.004	0	-	-
Cadmium (Cd)	0.005	0	-	-
Chromium (Cr)	0.1	0	-	-
Copper (Cu)	1.3	0	-	-
Fluoride (F)	4.0	3	4.8	skeletal damage
Lead (Pb)	0.015	0	-	-
Mercury (Hg)	0.002	0	-	-
Nickel (Ni)	0.1	0	-	-
Selenium (Se)	0.05	0	-	-
Thallium (Tl)**	0.002	0	-	-
Radiochemistry Constituents				
Gross Alpha	15	0	-	-
Ra-226+Ra-228	5	0	-	-
Radon **	300	3	989	cancer
Radon **	4,000	0	-	-
Uranium	30	1	-	-

All units are mg/L except gross alpha, radium-226+228 and radon (pCi/L), and uranium (ug/L).

* Health-based drinking water quality standards are based on a lifetime consumption of two liters of water per day over a 70-year life span.³⁶

** Proposed EPA Safe Drinking Water Act standards for radon in drinking water.³⁷

Inorganic Results

Of the seven sites sampled for the full suite of inorganic constituents (excluding radionuclide sample results), one site (14 percent) met all health-based and aesthetics-based, water quality standards.

Health-based Primary MCL water quality standards were exceeded at three sites (43 percent) (Figure 8; Table 4). Constituents above Primary MCLs include arsenic (three sites) and fluoride (three sites).

Potential health impacts of these Primary MCL exceedances are also provided in Table 4.

Aesthetics-based Secondary MCL water quality guidelines were exceeded at eight sites (86 percent; Figure 8; Table 5). Constituents above Secondary MCLs include fluoride (four sites), total dissolved solids (TDS) (three sites) and one site apiece for aluminum, chloride, iron, manganese, and sulfate.

Potential health impacts of these Secondary MCL exceedances are given in Table 5.

Table 5 - Sites Exceeding Aesthetics-based Water Quality Guidelines/Secondary MCLs

Constituents	Secondary MCL	Number of Sites Exceeding Secondary MCLs	Maximum Concentration	Aesthetic Effects of MCL Exceedances
Physical Parameters				
pH - field	< 6.5	0	-	bitter metallic taste; corrosion
pH - field	> 8.5	6	9.21	slippery feel; soda taste; deposits
General Mineral Characteristics				
TDS	500	95	20,000	hardness; deposits; colored water; staining; salty taste
Major Ions				
Chloride (Cl)	250	77	5,900	salty taste
Sulfate (SO ₄)	250	62	8,200	salty taste
Trace Elements				
Aluminum (Al)	0.05 to 0.2	0	-	colored water
Fluoride (F)	2.0	65	9.55	tooth discoloration
Iron (Fe)	0.3	14	0.946	rusty color; sediment; metallic taste; staining
Manganese (Mn)	0.05	22	4.45	black to brown color; black staining; bitter metallic taste
Silver (Ag)	0.1	0	-	-
Zinc (Zn)	5.0	0	-	metallic taste

All units mg/L except pH is in standard units (su).

Radionuclide Results

Of the four sites sampled for radionuclides, there was one health-based Primary MCL water quality standards for uranium.

Radon Results

The five sites sampled for radon had the following water quality results (Map 4):

The proposed 4,000 picocuries per liter (pCi/L) standard that would apply if Arizona establishes an enhanced multimedia program to address the health risks from radon in indoor air was not exceeded at any sites.

The proposed 300 pCi/L standard that would apply if Arizona doesn't develop a multimedia program was exceeded at three sites (60 percent).³⁸

Analytical Results

Analytical inorganic and radiochemistry results of the Western Mexican Drainage basin sample sites are summarized (Table 6 and Table 7) using the following indices: MRLs, the number of sample sites over the MRL, upper and lower 95 percent confidence intervals (CI_{95%}), median, and mean.

Confidence intervals are a statistical tool which indicates that 95 percent of a constituent's population lies within the stated confidence interval.³⁴

Specific constituent information for each sampled groundwater site is in Appendix B.



Figure 9 - ADEQ's Elizabeth Boettcher admiring Quitobaquito Spring in the Organ Pipe Cactus National Monument. The sample (WMD-3) exceeded water quality standards for arsenic, fluoride, and uranium.

Table 6 - Summary Statistics for Groundwater Quality Data

Constituent	Minimum Reporting Limit (MRL)**	# of Samples / Samples Over MRL	Median	Lower 95% Confidence Interval	Mean	Upper 95% Confidence Interval
Physical Parameters						
Temperature (°C)	0.1	7 / 7	26.9	20.1	25.3	30.5
pH-field (su)	0.01	7 / 7	7.66	7.55	7.79	8.04
pH-lab (su)	1.68	7 / 7	8.02	7.92	7.65	8.20
General Mineral Characteristics						
T. Alkalinity	6.0	7 / 7	170	132	222	313
SC-field (µS/cm)	N/A	7 / 7	830	91	1184	2277
SC-lab (µS/cm)	2.0	7 / 7	770	112	1166	2218
Hardness-lab	13	7 / 7	97	35	119	204
TDS-field	N/A	7 / 7	539	59	770	1482
TDS-lab	20	7 / 7	490	58	744	1429
Major Ions						
Calcium	1	7 / 7	38	13	34	55
Magnesium	1	7 / 6	8.3	2.1	10.1	18
Sodium	0.5	7 / 7	160	4	213	421
Potassium	0.5	7 / 7	3.5	2.6	3.4	4.3
Bicarbonate	6.0	7 / 7	207	159	270	382
Carbonate	6.0	7 / 0		> 75 percent of data below MRL		
Chloride	2	7 / 7	100	-18	156	331
Sulfate	2	7 / 7	68	-85	151	389
Nutrients						
Nitrate (as N)	0.1	7 / 6	25	0.4	2.3	4.2
Nitrite (as N)	0.1	7 / 0		> 75 percent of data below MRL		
TKN	0.2	7 / 4		> 75 percent of data below MRL		
Ammonia	0.05	7 / 1		> 75 percent of data below MRL		
T. Phosphorus	0.1	7 / 2		> 75 percent of data below MRL		

All units mg/L except where noted.

Table 7 - Summary Statistics for Groundwater Quality Data

Constituent	Minimum Reporting Limit (MRL)*	# of Samples / Samples Over MRL	Median	Lower 95% Confidence Interval	Mean	Upper 95% Confidence Interval
Trace Elements						
Aluminum	0.2	7 / 1		> 75 percent of data below MRL		
Antimony	0.0001	7 / 0		> 75 percent of data below MRL		
Arsenic	0.0005	7 / 6	0.008	0.001	0.012	0.023
Barium	0.002	7 / 7	0.025	0.001	0.065	0.131
Beryllium	0.005	7 / 0		> 75 percent of data below MRL		
Boron	0.1	7 / 7	0.62	0.16	0.60	1.0
Cadmium	0.5	7 / 0		> 75 percent of data below MRL		
Chromium	0.002	7 / 5		> 75 percent of data below MRL		
Copper	0.0005	7 / 3		> 75 percent of data below MRL		
Fluoride	0.1	7 / 6	2.3	0.8	2.6	4.5
Iron	0.2	7 / 1		> 75 percent of data below MRL		
Lead	0.005	7 / 1		> 75 percent of data below MRL		
Manganese	0.15	7 / 1		> 75 percent of data below MRL		
Mercury	0.0002	7 / 0		> 75 percent of data below MRL		
Nickel	0.005	7 / 1		> 75 percent of data below MRL		
Selenium	0.01	7 / 5		> 75 percent of data below MRL		
Silver	0.002	7 / 0		> 75 percent of data below MRL		
Strontium	0.01	7 / 6	0.33	0.11	0.37	0.63
Thallium	0.002	7 / 0		> 75 percent of data below MRL		
Zinc	0.0125	7 / 6		> 75 percent of data below MRL		
Radiochemical						
Gross α (pCi/L)	1	4 / 4	0.8	0.1	1.0	1.9
Uranium (ug/L)	1	4 / 4	10.6	-7.8	14.5	36.8
Radon (pCi/L)	1	5 / 5	417	-77	420	917
Isotopes						
O-18 (0/00)	Varies	7 / 7	-8.3	-8.9	-7.5	-6.3
D (0/00)	Varies	7 / 7	-58.8	-62.6	-54.5	-46.3
$\delta^{15}\text{N}$ (0/00)	Varies	7 / 7	9.0	6.9	10.1	13.2

Groundwater Composition

General Summary

Water chemistry in the Western Mexican Drainage basin was predominantly sodium-mixed (five sites). The other two samples were of sodium-chloride and mixed-bicarbonate

chemistry (Figure 10 – middle diagram) (Figure 11).

The dominant cation was sodium at six sites (Diagram 2 – left figure). The dominant anion was mixed at six sites (Figure 10 – right diagram).

The distribution of water chemistry throughout the basin is shown in Figure 10.

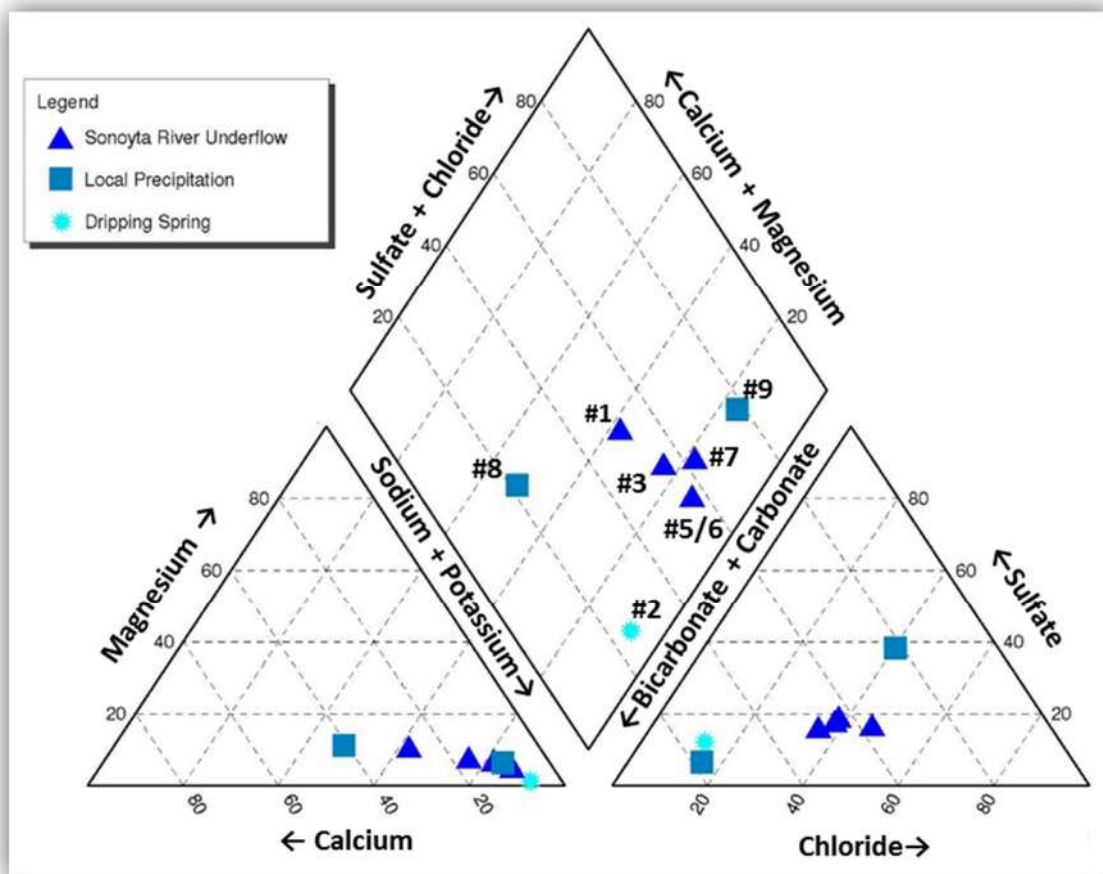


Figure 10 - Samples collected in the Western Mexican Drainage basin are predominantly of sodium-mixed chemistry.

Map 3 - Water Chemistry

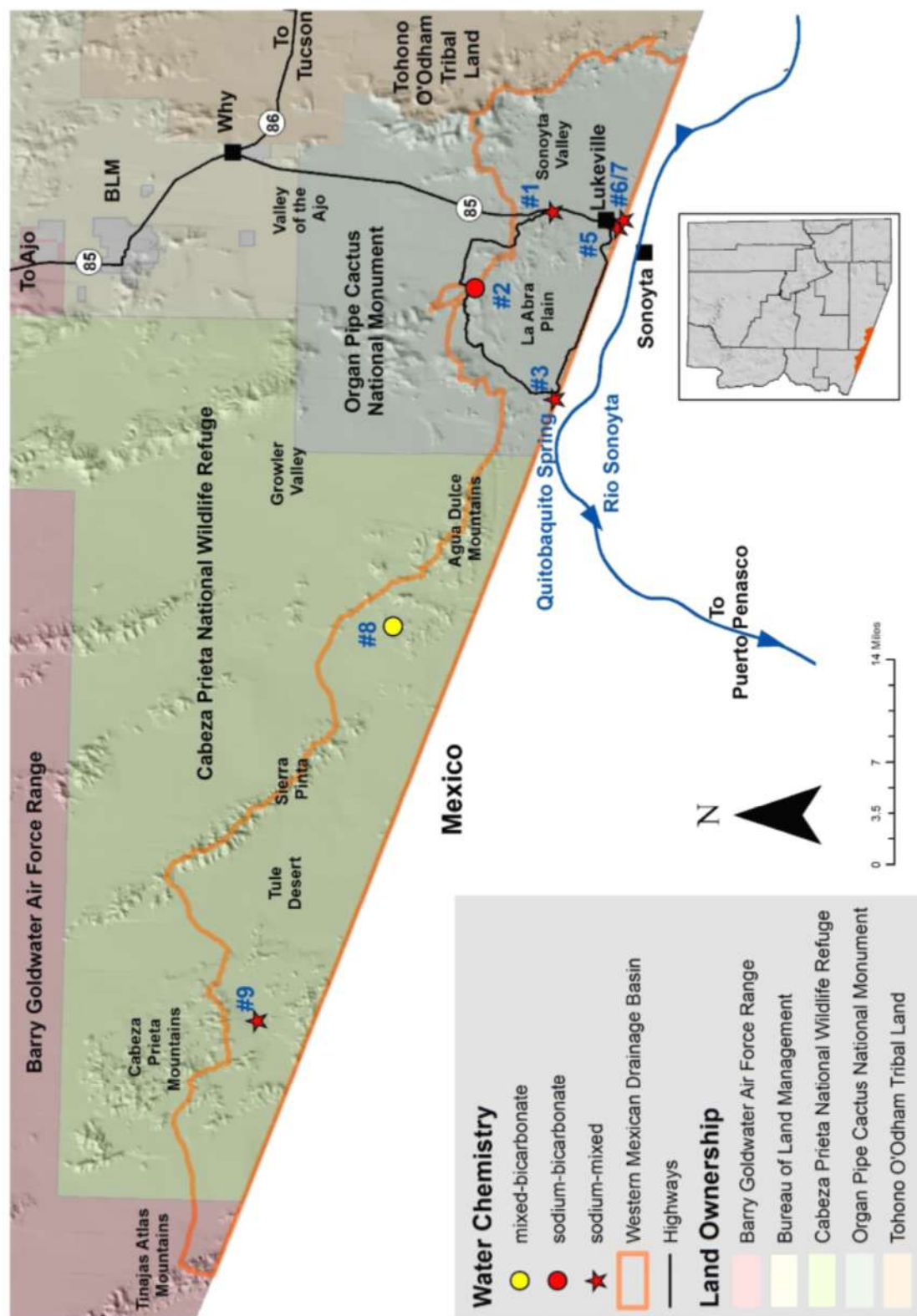


Figure 11 – Water Chemistry of the Western Mexican Drainage basin.

At five sites, levels of pH-field were *slightly alkaline* (7 - 8 su), and two sites were *moderately alkaline* above 8 su.¹²

TDS concentrations were considered *fresh* (below 999 mg/L) at six sites and *slightly saline* (1,000 to 3,000 mg/L) at one site (Figure 12).¹²

Hardness concentrations were *soft* (below 75 mg/L) at two sites, *moderately hard* (75 – 150 mg/L) at four sites, and *hard* (150 – 300 mg/L) at one site (Figure 13).¹⁰

Nitrate (as nitrogen) concentrations at most sites may have been influenced by human activities according to a prominent nationwide USGS study.²² Nitrate concentrations were divided into natural background (one site at < 0.2 mg/L), may or may not indicate human influence (three sites at 0.2 – 3.0 mg/L), and may result from human activities (three sites at 3.0 – 10 mg/L).¹⁷

Most trace elements such as aluminum, antimony, beryllium, cadmium, copper, iron, lead, manganese, mercury, nickel, silver, and thallium were rarely detected. Only arsenic, barium, boron, chromium, fluoride, strontium, and zinc were detected at more than 50 percent of the sites.

The groundwater at each sample site was assessed as to its suitability for irrigation use based on salinity and sodium hazards. Excessive levels of sodium are known to cause physical deterioration of the soil and vegetation. Irrigation water may be classified using SC and the Sodium Adsorption Ratio (SAR) in conjunction with one another.³³

Groundwater sites in the Western Mexican Drainage basin display a wide range of irrigation water classifications. Samples predominantly had a “medium” sodium hazard and a “medium” to “high” salinity hazard (Table 8).

Table 8 - Sodium and Salinity Hazards for Sample Sites

Hazard	Total Sites	Low	Medium	High	Very High
Sodium Hazard					
Sodium Adsorption Ratio (SAR)		0 - 10	10- 18	18 - 26	> 26
Sample Sites	7	2	4	0	1
Salinity Hazard					
Specific Conductivity (µS/cm)		0–250	250 – 750	750-2250	>2250
Sample Sites	7	0	3	3	1

Map 4 - Total Dissolved Solids (TDS)

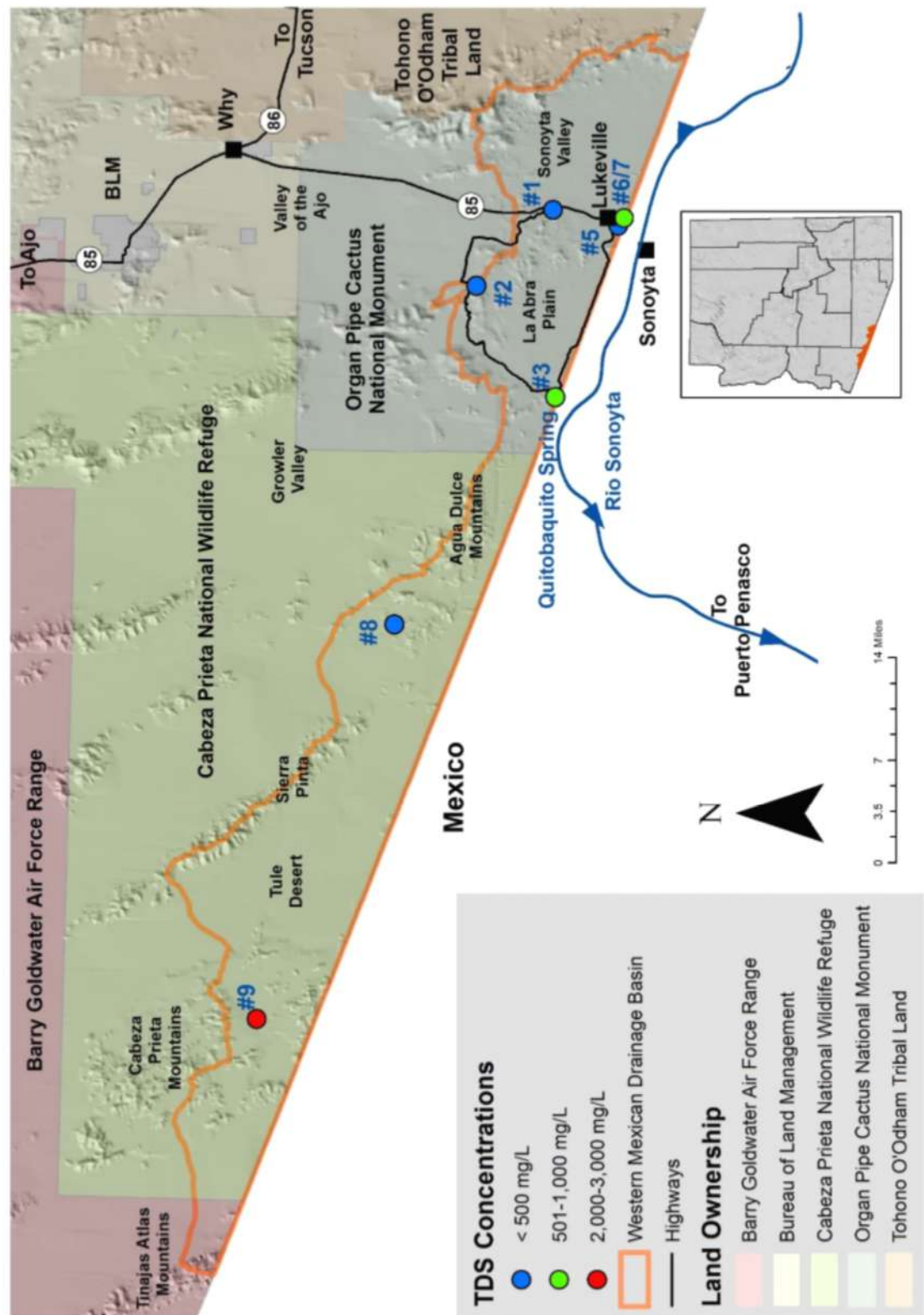


Figure 12 - TDS concentrations in the Western Mexican Drainage basin.

Map 5 - Hardness

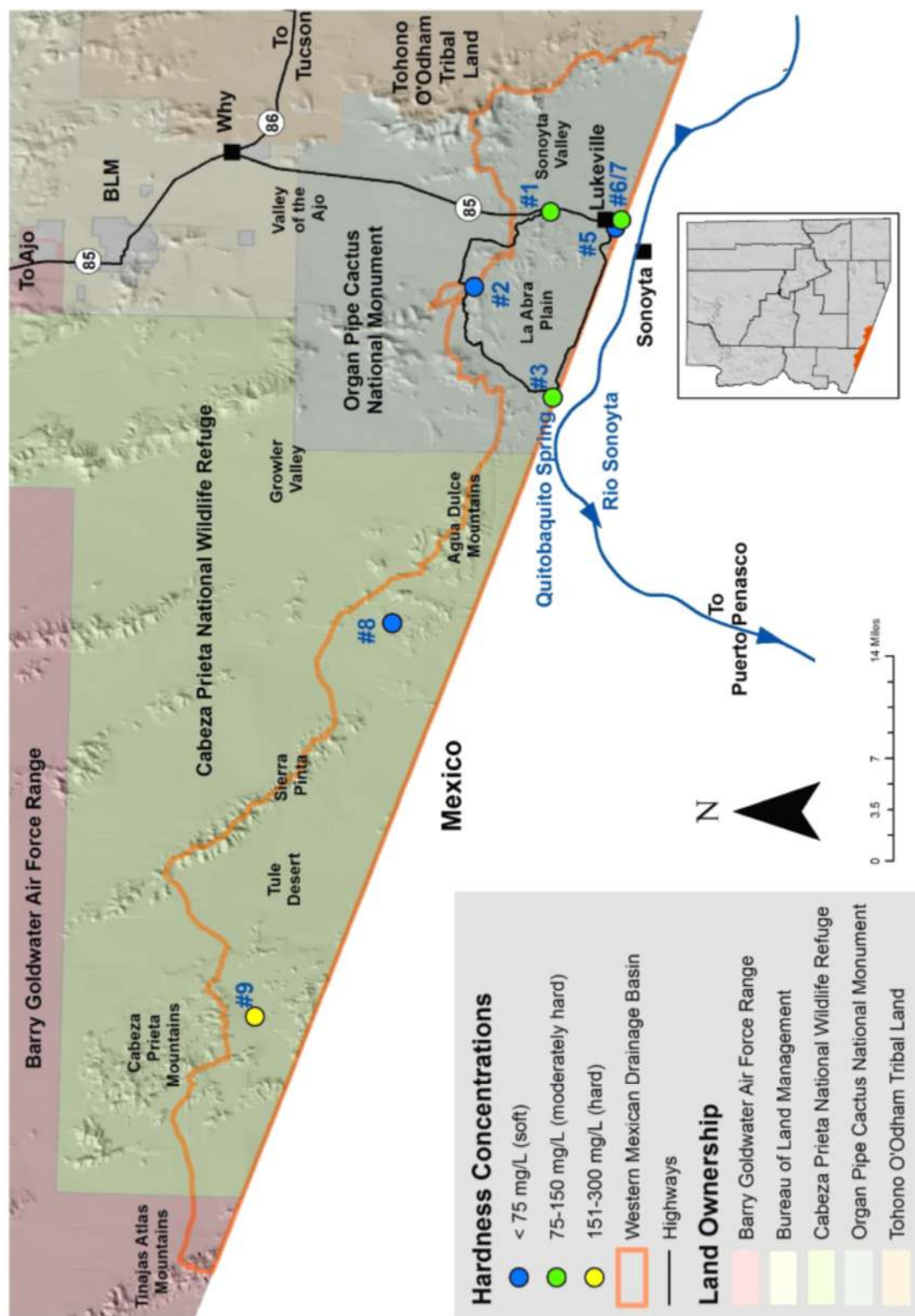


Figure 13 - Hardness concentrations in the Western Mexican Drainage basin.

Oxygen and Hydrogen Isotopes

Oxygen and hydrogen isotope samples were collected from seven sites. The evaporation line formed by the samples (Figure 14) is described by the linear equation: $\delta D = 5.6^{18}O + -12.8$.

Values of $\delta^{18}O$ and δD at four sites are lower than would be expected from recharge occurring at elevations within the basin. In addition to local precipitation, these samples likely reflect underflow from precipitation that occurred in the higher-elevation headwaters of the Rio Sonoyta, either in the Sierra de El Cobre in Sonora, Mexico or from the Baboquivari Range in the eastern part of the Tohono O'odham Nation.

The samples collected from two wells located on the Cabeza Prieta National Wildlife Refuge, Papago Well (WMD-8) and Tule Well (WMD-9), have higher values than the previous samples. These sites match the average values of local precipitation in the area.

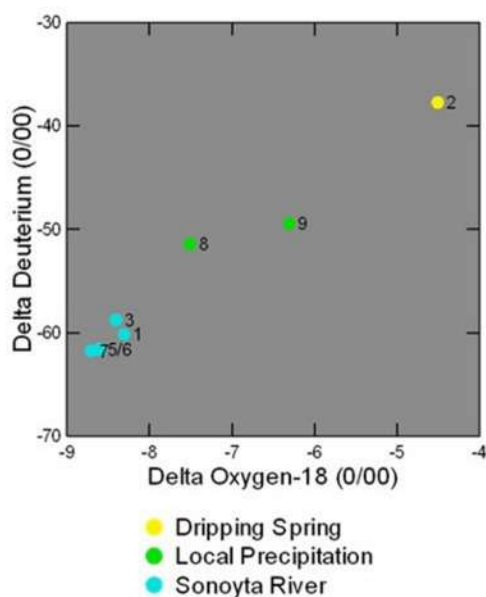


Figure 14 - Evaporation line for the basin.

Oxygen and Hydrogen Isotopes

Groundwater characterizations using oxygen and hydrogen isotope data may be made with respect to the climate and/or elevation where the water originated, residence within the aquifer, and whether or not the water was exposed to extensive evaporation prior to collection. This is accomplished by comparing oxygen-18 isotopes ($\delta^{18}O$) and deuterium (δD), an isotope of hydrogen, data to the Global Meteoric Water Line (GMWL).

The GMWL is described by the linear equation:

$$\delta D = 8 \delta^{18}O + 10$$

where δD is deuterium in parts per thousand (per mil, ‰), 8 is the slope of the line, $\delta^{18}O$ is oxygen-18 ‰, and 10 is the y-intercept. The GMWL is the standard by which water samples are compared and is a universal reference standard based on worldwide precipitation without the effects of evaporation.

A Local Meteoric Water Line (LMWL) is created using rainfall for a particular location. Data for the whole year, over the course of many years, tend to plot not too far from the GMWL (slope of 8, intercept 10), although this varies by region and is affected by varying climatic and geographic factors.

Groundwater from arid environments is typically subject to evaporation, which enriches δD and $\delta^{18}O$, resulting in a lower slope value (usually between 3 and 6) as compared to the slope of 8 associated with the GMWL (Figure 15).

Dripping Springs (WMD-2), located within the national monument, is the most evaporated. Evaporation may have occurred before infiltration or after discharge at the spring. The spring is open to the surface, so it might also receive direct recharge from precipitation

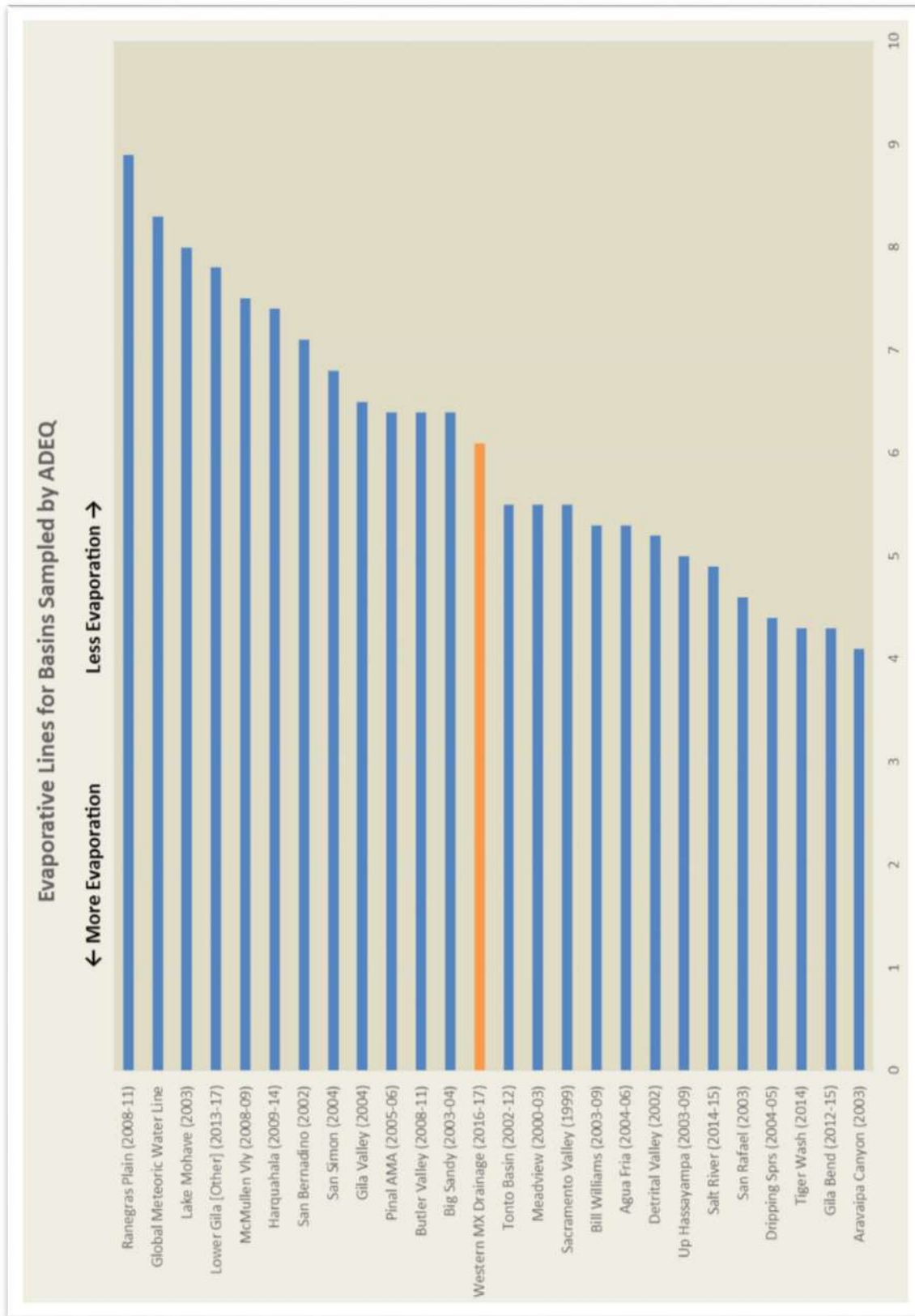


Figure 15 - Evaporation lines from ADEQ Ambient Groundwater Studies in Arizona.

Map 6 - Recharge Source

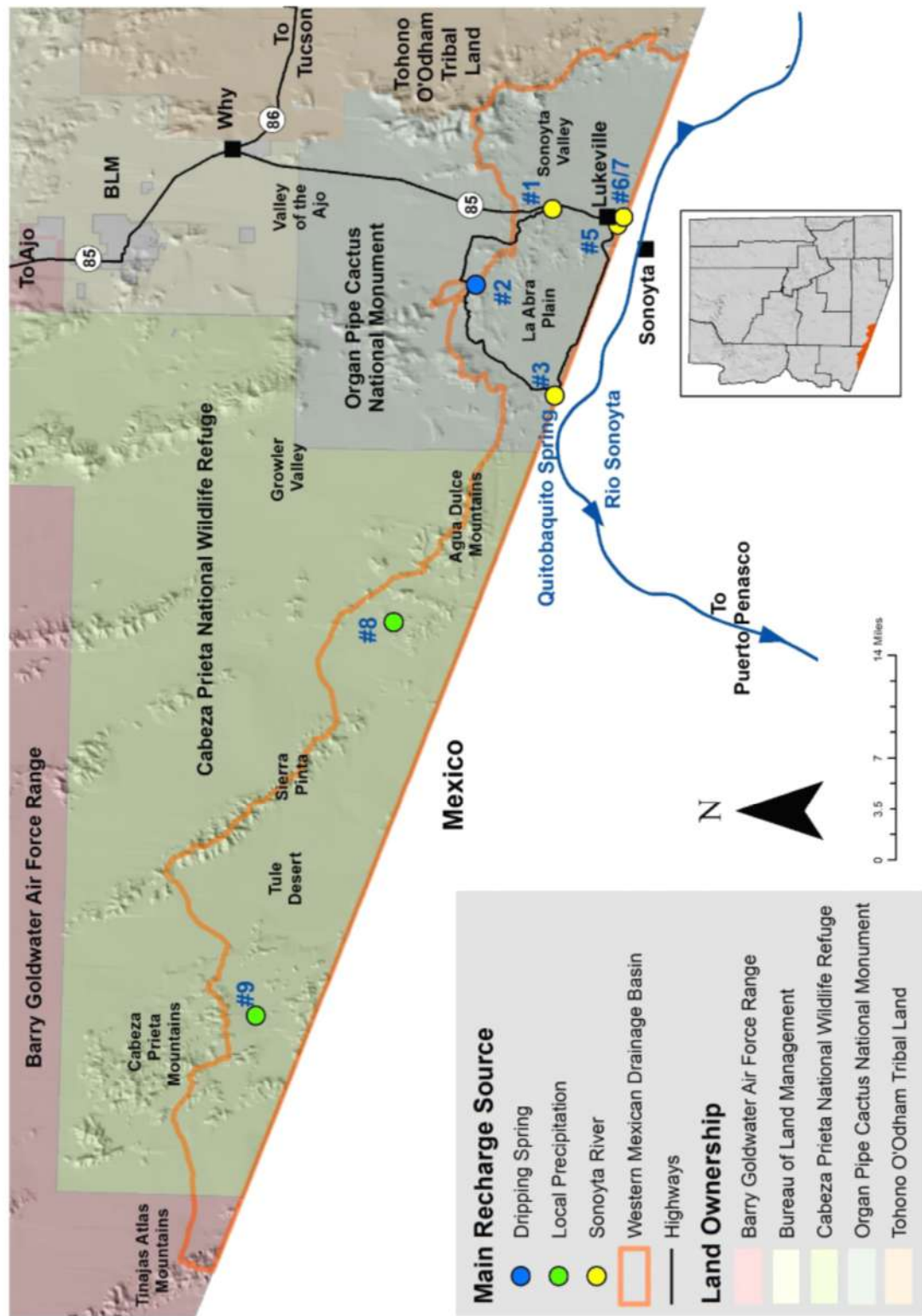


Figure 16 - Recharge source of samples in the Western Mexican Drainage basin.

(Figure 7). If the precipitation occurs during the summer monsoon season, it would also result in higher $\delta^{18}\text{O}$ and δD values as summer rainfall has higher values and evaporation is more intense during the summer months.

Nitrogen Isotopes

Sources of nitrate in groundwater may be distinguished by measuring two stable isotopes of nitrogen, nitrogen-14, and nitrogen-15, often represented by $\delta^{15}\text{N}$. Although the percentage of the two isotopes is nearly constant in the atmosphere, certain chemical and physical processes preferentially utilize one isotope, causing a relative enrichment of the other isotope in the remaining reactants.

Groundwater samples for $\delta^{15}\text{N}$ analysis were collected at seven sites. The $\delta^{15}\text{N}$ values ranged from 5.8 ‰ to +16.7 ‰ (Figure 17). Nitrate values ranged from non-detect to 4.5 mg/L (Figure 18).

Because of these isotopic fractionation processes, nitrate from different nitrogen sources has been shown to have different N isotope ratios. The $\delta^{15}\text{N}$ values have been cited as ranging from +2 to +9 per mil for natural soil organic matter sources, -3 to +3 for inorganic fertilizer sources, +10 to +20 per mil for animal waste.^{xxxix}

The $\delta^{15}\text{N}$ results in the basin are distributed in the following categories:

Organic soil matter (+2 to +9) – four sites,

Fertilizer (-3 to +3) – zero sites,

Animal waste (+10 to +20) – two sites,

Undetermined (+9 to +10) – one site

Undetermined (> +20) – no sites

Based on these results, it appears that the nitrogen source is predominantly organic soil matter and animal waste.

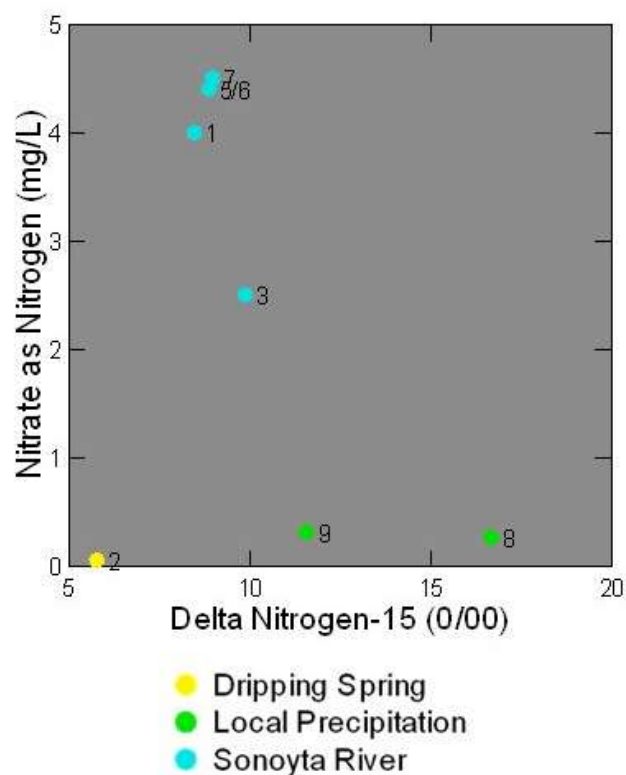


Figure 17 - Nitrate-Nitrogen-15 Relationship.

Based on seven sites sampled in the Western Mexican Drainage basin, elevated nitrate (as nitrogen) concentrations are correlated to recharge originating in higher elevations at the headwaters of the Rio Sonoyta.

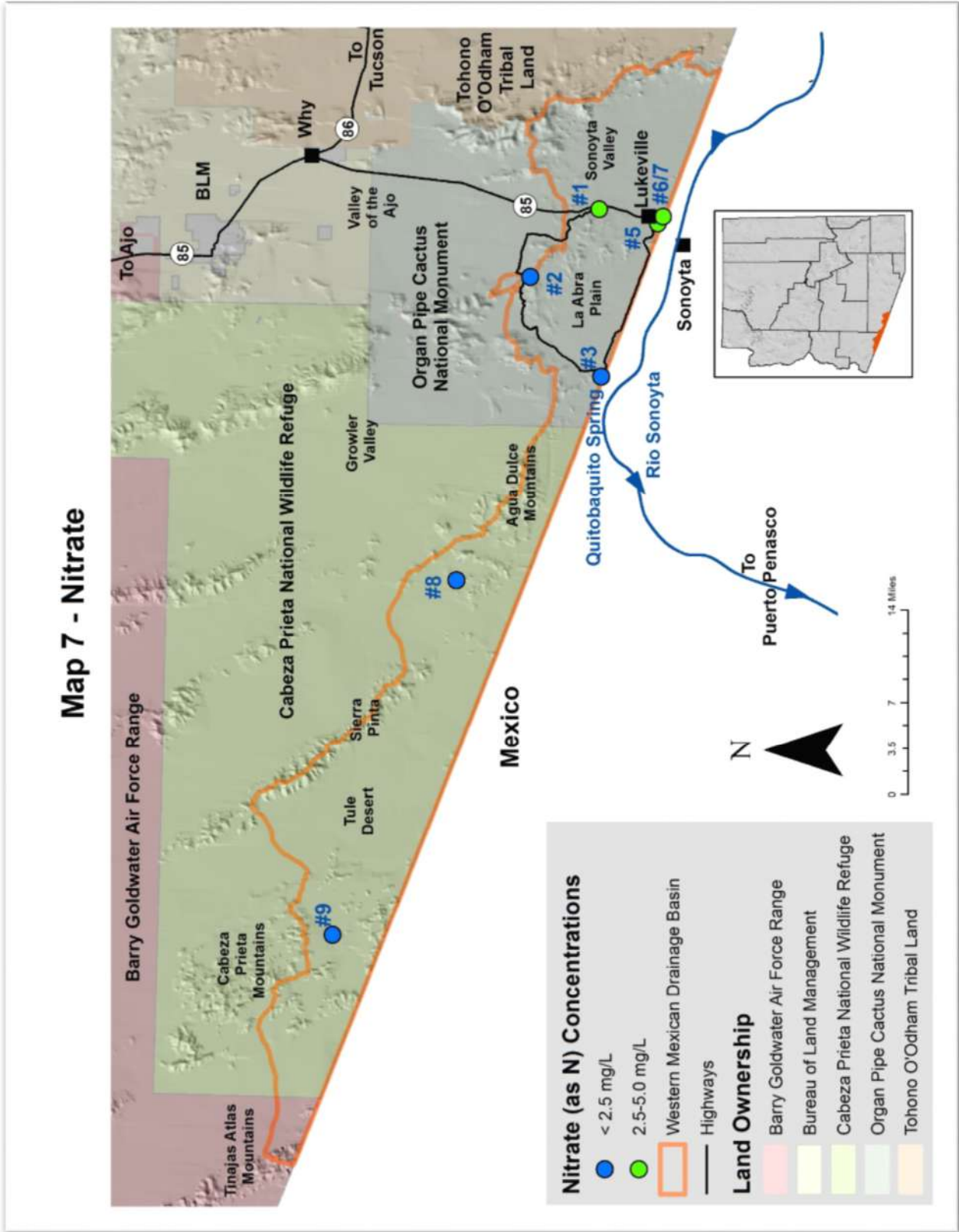


Figure 18 - Nitrate concentrations in the Western Mexican Drainage basin.

Discussion

The Western Mexican Drainage basin contains 610 square miles within Yuma and Pima counties in southwestern Arizona. The basin comprises a thin strip of land, no more than 15 miles wide, along the international boundary with Mexico. The majority of the Western Mexican Drainage basin lies within Mexico.

Land ownership consists of federal lands (99 percent) including the Cabeza Prieta National Wildlife Refuge, and the Organ Pipe Cactus National Monument.

Groundwater in the basin is commonly sodium-mixed chemistry, slightly-alkaline, fresh, and moderately hard.^{40 41}

Water Quality Standards - The results of the ADEQ groundwater quality revealed that 43 percent of wells sampled had health-based water quality standard exceedances including arsenic, fluoride, and uranium. These are common contaminants found in groundwater throughout the state.⁴²

Aesthetics-based water quality constituents were exceeded at 86 percent of sample sites. Constituents exceeded include fluoride (four sites) TDS (three sites) and at one site apiece for aluminum, chloride, iron, manganese, and sulfate.

One of the seven sites met all drinking water quality standards (Figure 19).

Groundwater in some areas of the Western Mexican Drainage basin, such as near the community of Lukeville, is generally not suitable for drinking water uses without treatment based on the sampling results from this study.

Arsenic - Arsenic exceeded health-based, water quality standards in three samples, with 0.029 mg/L the highest concentration (Figure 20). Arsenic concentrations are affected by reactions with hydroxyl ions and are influenced by factors such as an oxidizing environment, lithology, and aquifer residence time.⁴³



Figure 19 – Papago Windmill, located in by the O’Neill Hills within the Cabeza Prieta National Wildlife Refuge, was the only sample site (WMD-8) to meet all water quality standards. Solar energy is used to pump groundwater at the former windmill.

Map 8 - Arsenic

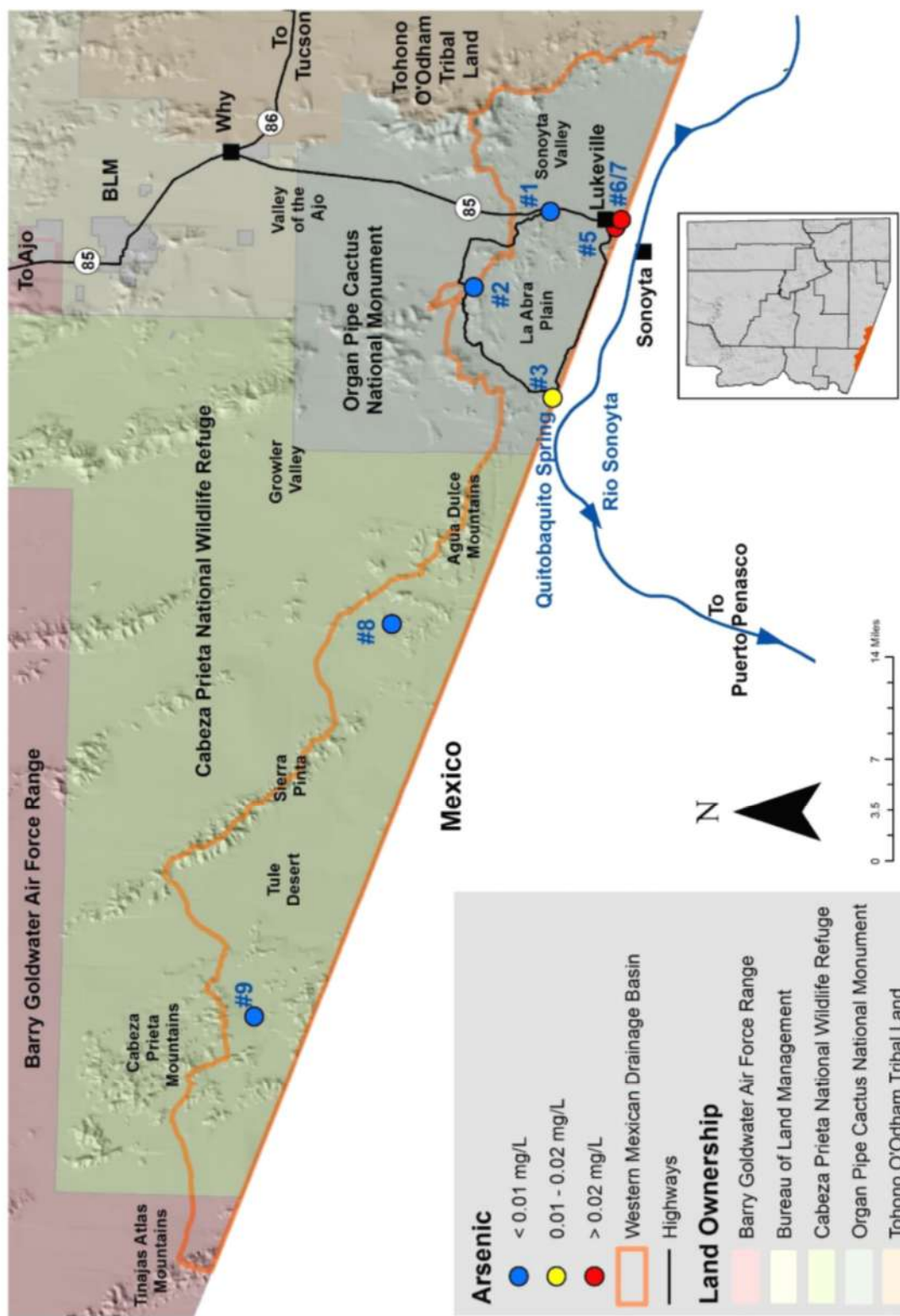


Figure 20 - Arsenic concentrations in the Western Mexican Drainage basin.



Figure 21 - Most of the Western Mexican Drainage basin is so remote, water sources such as Papago Well are major landmarks.

Fluoride - Fluoride exceeded the 4.0 mg/L health-based, water quality standards in samples collected from three wells, with concentrations as high as 4.8 mg/L (Figure 22). The three wells with fluoride exceedances also had arsenic exceedances, as elevated concentrations of these two constituents frequently occur together. The 2.0 mg/L aesthetic-based Secondary MCL for fluoride was exceeded at four wells.

Fluoride concentrations in groundwater are often controlled by calcium through precipitation or dissolution of the mineral fluorite. In a chemically closed hydrologic system, calcium is removed from solution by precipitation of calcium carbonate and the formation of smectite clays.

Concentrations exceeding 5 mg/L of dissolved fluoride may occur in groundwater depleted in calcium if a source of fluoride ions is available for dissolution.⁴⁴

Sites only partially depleted in calcium may be controlled by processes other than fluorite dissolution. Hydroxyl ion exchange or sorption-desorption reactions have also been cited as providing controls on lower (< 5 mg/L) levels of fluoride. As pH values increase downgradient, greater levels of hydroxyl ions may affect an exchange of hydroxyl for fluoride ions thereby increasing fluoride in solution.⁴⁵

Fluoride concentrations were higher in recharge supplied by the Sonoyta River than in local precipitation.

Map 9 - Fluoride

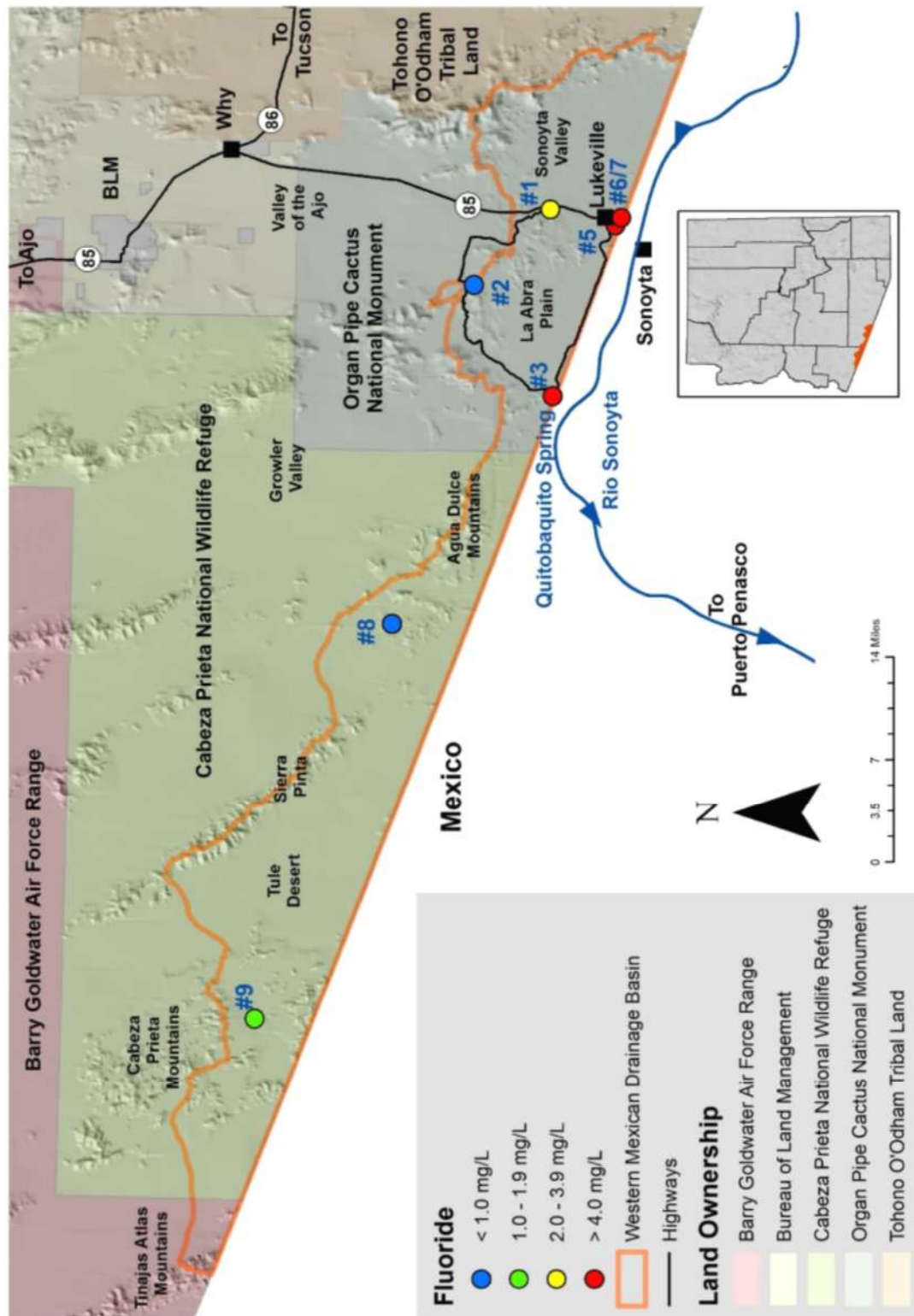


Figure 22 - Fluoride concentrations in the Western Mexican Drainage basin.

Uranium - Uranium exceeded the 30.0 ug/L health-based, water quality standards in one sample collected from Quitobaquito Spring. Uranium exceedances may be caused by weathering of rocks or sediments, especially granite which composes the Quitobaquito Hills from which issues Quitobaquito Spring.⁴⁶

Recharge Source - The collection of stable isotopes of oxygen-18 and hydrogen samples at sites in the Western Mexican Drainage basin assisted in determining the sources of recharge to the basin. Particularly important was the improved understanding of the groundwater sources that supply Quitobaquito Spring, perhaps the most ecologically important spring in southwestern Arizona (Figure 23).

Previous studies indicated that Quitobaquito Spring was a fissure spring, with its source located below the local water table. The spring was thought to be supplied by a groundwater flow system along Agaujita Wash, located to the north. The spring was also speculated to be hydraulically connected to the regional aquifer system in Mexico.⁴⁷

The stable isotopes of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ collected at Quitobaquito Spring confirm the influence of the regional aquifer supplied by surface flow or underflow from the Rio Sonoyta. This determination is based on the higher values that indicate a contribution from less-evaporated precipitation from the higher-elevation headwaters of the Ro Sonoyta.⁴⁸



Figure 23 - Quitobaquito Spring is just across the international border, which parallels Mexican Highway 2 at this location.

Besides receiving discharge from precipitation in the Sierra de El Cobre in Sonora, two major washes in the U.S., both located within the Tohono O'odham Nation, Vamori Wash and San Simon Wash, flow into the Rio Sonoyta.

The additional certainty about the source of Quitobaquito Spring indicates that Organ Pipe Cactus National Monument should monitor how groundwater withdrawals in Mexico impact the flow to assure the vital water source's continued viability.

For drinking water uses, from the limited data collected, suggests that local precipitation is the preferred recharge source for public or domestic water users (Table 12). However, recharge from the Sonoyta River does provide the public water supply well (WMD-1) used by the Organ Pipe Cactus National Monument, which meets health-based water quality standards (Figure 24).



Figure 24 - ADEQ's Elizabeth Boettcher samples South Well #4 used for public water supply at the Organ Pipe Cactus National Monument.

Table 9 - Water Quality Standard Exceedances by Recharge Source

Recharge Source	Number of Sites Exceeding Primary Standards	Number of Sites Exceeding Only Secondary Standards	Number of Sites Without Standard Exceedances
Dripping Springs	0	1	9
Local Precipitation	0	1	1
Sonoyta River	3	1	0
Total	3	3	1

Appendix A. Data for Sample Sites, Western Mexican Drainage, 2016-2017

Site #	Cadastral / Pump Type	Latitude - Longitude	ADWR #	ADEQ #	Site Name	Samples Collected	Well Depth	Water Depth	Sub-basin
1st Field Trip, February 23, 2016 – Towne & Boettcher									
WMD-1	C(17-5)17acb submersible	31.9496 -112.8016	632188	25676	South Well #4	Inorganic, Radiochem Radon, O,H, N isotope	430'	310'	
2nd Field Trip, January 9-10, 2017 – Towne & Boettcher									
WMD-2	C(16-6)21bab spring	32.024196 -112.89189	-	25660	Dripping Springs	Inorganic O,H, N isotope	-	-	
WMD-3	C(17-7)18dac spring	31.94404 -113.019199	-	25685	Quitobaquito Spring	Inorganic, Radiochem O,H, N isotope	-	-	
WMD-5/6	C(18-5)06ddc submersible	31.88135 -112.81596	807672	25698	Lukeville POE Well	Inorganic Radon, O,H, N isotope	150'	65'	
WMD-7	C(18-5)06ddd submersible	31.88143 -112.81454	219667	81314	Gringo Pass Motel Well	Inorganic Radon, O,H, N isotope	300'	100'	
3rd Field Trip, February 28, 2017 – Towne & Boettcher									
WMD-8	C(15-10)22dcc submersible	32.099083 -113.286861	627133	25652 25653	Papago Well	Inorganic, Radiochem Radon, O,H, N isotope	400'	201'	
WMD-9	C(14-14)07bad submersible	32.099083 -113.286861	-	25644	Tule Well	Inorganic, Radiochem Radon, O,H, N isotope	40'	-	

Appendix B. Groundwater Quality Data, Western Mexican Drainage Basin, 2016-

Site #	MCL Exceedances	Temp (°C)	pH-field (su)	pH-lab (su)	SC-field (µS/cm)	SC-lab (µS/cm)	TDS-f (mg/L)	TDS (mg/L)	Hard (mg/L)
WMD-1	F	31.7	7.66	8.02	781	770	507	476	97.2
WMD-2	Fe, Mn, Al	13.5	8.17	7.5	246	430	161	300	13
WMD-3	TDS, As, F , U	24.7	7.61	7.6	1152	1100	749	670	140
WMD-5/6	As, F	27.5	7.96	8.15	830	750	539	490	56.5
WMD-7	TDS, As, F	25.8	8.05	8.2	946	870	615	540	88
WMD-8	-	27.0	7.44	7.8	549	540	357	330	140
WMD-9	TDS, Cl, SO ₄	26.9	7.66	8.2	3783	3700	2462	2400	300

italics = constituent exceeded holding time

bold = constituent concentration exceeded Primary or Secondary Maximum Contaminant Level

Appendix B. Groundwater Quality Data, Western Mexican Drainage Basin, 2016--Continued

Site #	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Potassium (mg/L)	T. Alk (mg/L)	Bicarbonate (mg/L)	Carbonate (mg/L)	Chloride (mg/L)	Sulfate (mg/L)
WMD-1	40.6	9.66	103	3.79	162	198	ND	82.8	52.0
WMD-2	5.1	ND	76	4.2	170	207	ND	21	26
WMD-3	38	11	200	4.6	250	305	ND	150	97
WMD-5/6	14	5.05	160	3.25	165	195	ND	100	68
WMD-7	22	8.3	180	3.5	160	195	ND	140	70
WMD-8	45	7.4	60	1.9	220	268	ND	31	17
WMD-9	73	28	710	2.8	430	525	ND	570	730

italics = constituent exceeded holding time

bold = constituent concentration exceeded Primary or Secondary Maximum Contaminant Level

Appendix B. Groundwater Quality Data, Western Mexican Drainage Basin, 2016--Continued

Site #	Nitrate-N (mg/L)	$\delta^{15}\text{N}$ (‰)	Nitrite-N (mg/L)	TKN (mg/L)	Ammonia (mg/L)	T. Phos. (mg/L)	SAR (value)	Irrigation Quality	Alum (mg/L)	Strontium (mg/L)
WMD-1	4.0	8.5	ND	ND	ND	0.030	4.5	C3-S1	ND	0.325
WMD-2	ND	5.8	ND	15	13	2.7	9.2	C2-S2	1.4	ND
WMD-3	2.5	9.9	ND	0.76	ND	ND	7.4	C3-S2	ND	0.48
WMD-5/6	4.4	8.9	ND	ND	ND	ND	9.3	C2-S2	ND	0.17
WMD-7	4.5	9.0	ND	ND	ND	ND	8.3	C3-S2	ND	0.27
WMD-8	0.26	16.7	ND	0.26	ND	ND	2.2	C2-S1	ND	0.35
WMD-9	0.31	11.6	ND	0.25	ND	ND	17.9	C4-S4	ND	0.92

italics = constituent exceeded holding time

bold = constituent concentration exceeded Primary or Secondary Maximum Contaminant Level

Appendix B. Groundwater Quality Data, Western Mexican Drainage Basin, 2016--Continued

Site #	Antimony (mg/L)	Arsenic (mg/L)	Barium (mg/L)	Beryllium (mg/L)	Boron (mg/L)	Cadmium (mg/L)	Chromium (mg/L)	Copper (mg/L)	Fluoride (mg/L)
WMD-1	ND	0.0082	0.0033	ND	0.434	ND	0.0049	ND	2.3
WMD-2	ND	0.0015	0.0018	ND	0.061	ND	0.00070	0.00075	ND
WMD-3	ND	0.012	0.025	ND	0.75	ND	0.0065	ND	4.5
WMD-5/6	ND	0.029	0.165	ND	0.615	ND	0.012	0.0018	4.8
WMD-7	ND	0.029	0.160	ND	0.65	ND	0.010	ND	4.6
WMD-8	ND	ND	0.079	ND	0.18	ND	ND	0.00089	0.40
WMD-9	ND	0.0036	0.020	ND	1.5	ND	ND	ND	1.8

italics = constituent exceeded holding time

bold = constituent concentration exceeded Primary or Secondary Maximum Contaminant Level

Appendix B. Groundwater Quality Data, Western Mexican Drainage Basin, 2016--Continued

Site #	Iron (mg/L)	Lead (mg/L)	Manganese (mg/L)	Mercury (mg/L)	Nickel (mg/L)	Selenium (mg/L)	Silver (mg/L)	Thallium (mg/L)	Zinc (mg/L)
WMD-1	ND	0.0013	ND	ND	0.0058	0.0020	ND	ND	0.0498
WMD-2	0.73	ND	0.33	ND	ND	ND	ND	ND	0.014
WMD-3	ND	ND	ND	ND	ND	0.0020	ND	ND	ND
WMD-5/6	ND	ND	ND	ND	ND	0.0018	ND	ND	0.0325
WMD-7	ND	ND	ND	ND	ND	0.0018	ND	ND	0.028
WMD-8	ND	ND	ND	ND	ND	ND	ND	ND	0.088
WMD-9	ND	ND	0.030	ND	ND	0.0085	ND	ND	0.130

italics = constituent exceeded holding time

bold = constituent concentration exceeded Primary or Secondary Maximum Contaminant Level

Appendix B. Groundwater Quality Data, Western Mexican Drainage Basin, 2016--Continued

Site #	Radon-222 (pCi/L)	Alpha (pCi/L)	Adj. Alpha (pCi/L)	Uranium (pCi/L)	Uranium (µg/L)	VOCs (µg/L)	* ¹⁸ O (‰)	* D (‰)	Type of Chemistry
WMD-1	989	8.4	0.6	7.8	9.1	-	-8.3	-60.2	sodium-mixed
WMD-2	-	-	-	-	-	-	-4.5	-37.8	sodium-bicarbonate
WMD-3	-	40.7	1.8	38.9	34.5	-	-8.4	-58.8	sodium-mixed
WMD-5/6	606	-	-	-	-	-	-8.6	-61.65	sodium-mixed
WMD-7	417	-	-	-	-	-	-8.7	-61.8	sodium-mixed
WMD-8	74	3.0	1.0	3.2	2.1		-7.5	-51.5	mixed-bicarbonate
WMD-9	15	14.1	0.6	13.5	12.2		-6.3	-49.5	sodium-mixed

LLD = Lower Limit of Detection

Italics = constituent exceeded holding time

References

- ¹ Arizona Department of Water Resources website, http://www.azwater.gov/AzDWR/StatewidePlanning/WaterAtlas/LowerColoradoRiver/documents/Volume_7_LGB_final.pdf, accessed 7/6/16.
- ² Ibid
- ³ Ibid
- ⁴ Environmental Protection Agency website, <https://www.epa.gov/your-drinking-water/table-regulated-drinking-water-contaminants>, accessed 4/18/16.
- ⁵ Heath, R.C., 1989, Basic ground-water hydrology: U.S. Geological Survey Water-Supply Paper, 84 p.
- ⁶ Crockett, J.K., 1995, Idaho statewide groundwater quality monitoring program-summary of results, 1991 through 1993: Idaho Department of Water Resources, Water Information Bulletin No. 50, Part 2, p. 60.
- ⁷ Email communication from Hector Alejandro Zamora, 05/09/2017.
- ⁸ Ibid
- ⁹ Ibid
- ¹⁰ <https://organpipehistory.com/orpi-a-z/quitobaquito-springs-2/>, accessed 9/26/26.
- ¹¹ Arizona Department of Environmental Quality, 2015-2016, Arizona Laws Relating to Environmental Quality: St. Paul, Minnesota, West Group Publishing, §49-221-224, p 134-137.
- ¹² ADWR Statewide Planning Water Atlas website, http://www.azwater.gov/azdwr/StatewidePlanning/WaterAtlas/CentralHighlands/documents/volume_5_SRB_final.pdf, accessed 9/18/2015.
- ¹³ ADWR, 1994.
- ¹⁴ ADWR, 1994.
- ¹⁵ <https://organpipehistory.com/orpi-a-z/quitobaquito-springs-2/>, accessed 9/26/26.
- ¹⁶ ADWR, 1994.
- ¹⁷ ADWR, 1994.
- ¹⁸ Arizona Department of Environmental Quality, 1991, Quality Assurance Project Plan: Arizona Department of Environmental Quality Standards Unit, 209 p.
- ¹⁹ Ibid

-
- ²⁰ Arizona Water Resources Research Center, 1995, Field Manual for Water-Quality Sampling: Tucson, University of Arizona College of Agriculture, 51 p.
- ²¹ Radiation Safety Engineering, Inc., 2015.
- ²² Personal communication from Test America staff 2017.
- ²³ Radiation Safety Engineering, Inc., 2015.
- ²⁴ University of Arizona Environmental Isotope Laboratory, 2015, personal communication from Christopher Eastoe.
- ²⁵ Ibid
- ²⁶ Arizona Department of Environmental Quality, 1991, Quality Assurance Project Plan: Arizona Department of Environmental Quality Standards Unit, 209 p.
- ²⁷ Arizona Water Resources Research Center, 1995, Field Manual for Water-Quality Sampling: Tucson, University of Arizona College of Agriculture, 51 p.
- ²⁸ Ibid
- ²⁹ Hem, J.D., 1985, Study and interpretation of the chemical characteristics of natural water [Third edition]: U.S. Geological Survey Water-Supply Paper 2254, 264 p.
- ³⁰ Ibid
- ³¹ Ibid
- ³² Environmental Protection Agency website, <https://www.epa.gov/your-drinking-water/table-regulated-drinking-water-contaminants>, accessed 4/18/16
- ³³ Arizona Department of Environmental Quality, 2014-2015, Arizona Laws Relating to Environmental Quality: Saint Paul, Minnesota, West Group Publishing, §49-221-224, pp. 134-137.
- ³⁴ Environmental Protection Agency website, <https://www.epa.gov/your-drinking-water/table-regulated-drinking-water-contaminants>, accessed 4/18/16
- ³⁵ Ibid
- ³⁶ Environmental Protection Agency website, <https://www.epa.gov/your-drinking-water/table-regulated-drinking-water-contaminants>, accessed 4/18/16
- ³⁷ U.S. Environmental Protection Agency website, <http://water.epa.gov/lawsregs/rulesregs/sdwa/radon/regulations.cfm>, accessed 3/18/16.
- ³⁸ U.S. Environmental Protection Agency website, <http://water.epa.gov/lawsregs/rulesregs/sdwa/radon/regulations.cfm>, accessed 3/18/16.
- ^{xxxix} Sustainability of Semi-Arid Hydrology and Riparian Areas website, <http://web.sahra.arizona.edu/programs/isotopes/nitrogen.html#2>
- ⁴⁰ Heath, R.C., 1989, Basic ground-water hydrology: U.S. Geological Survey Water-Supply Paper, 84 p.
- ⁴¹ Crockett, J.K., 1995, Idaho statewide groundwater quality monitoring program-summary of results, 1991 through 1993: Idaho Department of Water Resources, Water Information Bulletin No. 50, Part 2, p. 60.
- ⁴² Towne, D.C., and Jones, Jason, 2011, Groundwater quality in Arizona: a 15-year overview of the ADEQ ambient monitoring program (1995-2009): Arizona Department of Environmental Quality Open File Report 11-04., 44 p.
- ⁴³ Robertson, F.N., 1991, Geochemistry of ground water in alluvial basins of Arizona and adjacent parts of Nevada, New Mexico, and California: U.S. Geological Survey Professional Paper 1406-C, 90 p.
- ⁴⁴ Ibid
- ⁴⁵ Ibid
- ⁴⁶ Lowry, Jerry D. and Lowry, Sylvia B, 1988, "Radionuclides in Drinking Waters," in *American Water Works Association Journal*, July 1988.
- ⁴⁷ Carruth, R.L., 1996, Hydrogeology of the Quitobaquito Springs and La Abra Plain area, Organ Pipe Cactus National Monument, Arizona, and Sonora, Mexico: U.S. Geological Survey Water-Resources Investigations Report 95-4295, 23 p.
- ⁴⁸ Email communication from Hector Alejandro Zamora, 05/09/2017.